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Full Name of Author — Nom complet de l'auteur

ROBERT STEINBORN

Date of Birth — Date de naissance

DEC. 28/1954

Country of Birth — Lieu de naissance

CANADA

Permanent Address — Résidence fixe

426 RANCH GLEN PL / NW
CALGARY ALBERTA
T3G 1G3.

Title of Thesis — Titre de la thèse

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Name of Supervisor — Nom du directeur de thèse

DONALD L. FLOCK

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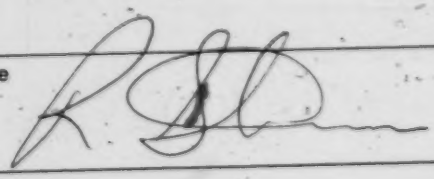

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The Rheological Behavior of Heavy Crude Oils and Their Emulsions

by

(C) Robert Steinborn

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

IN

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Robert Steinborn

PERMANENT ADDRESS 426 Ranch Glen Place NW.
Calgary, Alberta, Canada
T3G 1G3

DATED January 4, 1982

THE UNVERSITY OF ALBERTA

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled THE RHEOLOGICAL BEHAVIOR OF HEAVY CRUDE OILS AND THEIR EMULSIONS submitted by Robert Steinborn in partial fulfilment of the requirements for the degree of Master of Science in Petroleum Engineering.

.....

Dr. D.L. Flock (Supervisor)

.....

Dr. S.M. Farouq Ali

.....

Dr. R.E.D. McClung

DATE January 4, 1982

University of Alberta

To all my parents

Edward and Meta

and

John and Mary

and

my loving wife Maria

ABSTRACT

The rheological characteristics of two crude oils and their emulsions with water were studied using concentric cylinder and cone and plate rotational viscometers. Emulsions of oil-in-water and water-in-oil were formed with a rotational mixer and Triton X-100 as an emulsifier.

The effects of shear rate and temperature upon the flow characteristics of water-in-oil emulsions and the effect of shear rate on the flow characteristics of oil-in-water were determined.

The results show that emulsions exhibit Newtonian flow behaviour at low dispersed phase concentrations and pseudoplastic behaviour at higher concentrations. In addition, the viscosity is shown to be only slightly time dependent at higher shear rates.

It was noted that a large discontinuity in the viscosity occurs at disperse phase concentrations of 30 to 40% of the water-in-oil emulsions. This may be caused by a minor inversion of the water-in-oil emulsion to a dual water-in-oil-in-water emulsion. The viscosity of the dual emulsion would be lower because the water forms the continuous external phase.

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NOMENCLATURE

Parameter		Dimensions
a	Empirical Constant	-
a_m	Mean Distance Between Emulsion Droplets	L
d	Diameter of Emulsion Droplet	L
h	Effective Volume Coefficient	-
K	Empirical Constant	-
n	Flow Behavior Index	-
r	Mean Radius of a Droplet	L
S_c	Slippage Coefficient	-
t	Time	T
α	Coefficient of Proportionality (Emulsion - External Viscosities)	-
Γ	Emulsion Concentration (fraction)	-
Γ_{max}	Emulsion Concentration at Inversion	-
ϵ	Dielectric Constant of the Medium	-
ξ	Electrokinetic Potential	-
μ	Dynamic Viscosity	F T

μ_e	Dynamic Emulsion Viscosity	F T
μ_{ex}	Dynamic External Phase Viscosity	F T
μ_i	Dynamic Internal Phase Viscosity	F T
μ_{rel}	Relative Dynamic Viscosity - Emulsion Viscosity/External Phase Viscosity	-
ν	Kinematic Viscosity	$L^2 T^{-1}$
ρ	Fluid Density	$F T^2 L^{-4}$
ω	Angular Speed	T^{-1}
κ	Specific Conductivity	-
σ	Shear	T^{-1}
τ	Shear Stress	F
τ_y	Shear Stress Yield Value at 0 Shear Rate.	F

I. INTRODUCTION

A. BACKROUND

In the past, emulsion properties and emulsions themselves have only been of minor interest in oil recovery technology. With the major trend to enhanced oil recovery schemes, the use of emulsions to improve oil recovery has sparked interest to further understand emulsion behaviour flow properties.

Emulsion science has been developed by a range of industries, from paints to cosmetics and from foods such as milk products to pesticides. The rheologic properties and characteristics of emulsions have been of interest because of the many applications of emulsions. The oil producing industry can no longer merely consider emulsions as nuisances to be solved when they occur. Many researchers are now seeking to apply emulsions to improve the recovery of oil.

B. PURPOSE

The study of the rheological properties of crude oils and their emulsions was the broad objective of this study.

Specific objectives included:

1. Determine the rheology of both water-in-oil and oil-in-water emulsions of crude oil and distilled water.
2. To demonstrate that emulsion viscosity can be dependent

on the shear rate because of non-Newtonian behavior. More specifically, the emulsion can be non-Newtonian at some concentration and Newtonian at other concentrations.

3. To relate the emulsion viscosity as a function of shear rate, temperature and disperse phase concentration.

II. GENERAL FLOW CHARACTERISTICS AND RHEOLOGY

It is important, before dealing with emulsion flow, to outline the rheologic behavior which can exist.

The flow of fluids such as emulsions can be handled by a relationship such as the power-law model.

$$\tau = \mu \left[\frac{d\sigma}{dt}\right]^n \qquad (1.)$$

Where:

τ = Shear Stress (dyne/cm^2)

$d\sigma/dt$ = Shear Rate (sec^{-1})

μ = Viscosity (Pa.s)

n = Flow Index (dimensionless)

This equation relates the shear stress τ and the shear rate $d\sigma/dt$ using the constants μ, the coefficient of viscosity and n, the flow behavior index.

A. NEWTONIAN BEHAVIOR

In a Newtonian fluid the shear rate is directly proportional to the shear stress and a plot of shear rate vs. shear stress passes through the origin as shown in Figure 2.1. Alternatively, plotting the viscosity vs. shear rate, the viscosity of a Newtonian fluid would be a constant for all shear rates (see Figure 2.2).

B. NON-NEWTONIAN BEHAVIOR

The flow behavior of a non-Newtonian fluid can be described by any one of the following:

Pseudo Plastic

The shear rate vs. shear stress relationship of pseudoplastic fluids is shown in Figure 2.1. After a certain shear rate has been attained the fluid can approximate the linear relation of a Newtonian fluid.

The general shape of the shear rate vs. shear stress curve on log-log scale would be linear with a slope of less than 1, which implies that the flow index $n < 1$. A plot of viscosity vs. shear rate would display a decreasing viscosity for increasing shear rate (see Figure 2.2).

Bingham Plastic

A finite shear stress is required to initiate flow. The fluid behaves in a Newtonian manner after the initial shear stress (see Figure 2.1). A plot of viscosity vs. shear rate would appear very similar to the pseudoplastic case but the viscosity at 0 shear rate would be very large (see Figure 2.2). The equation for a plastic fluid is:

$$\tau - \tau_y = \mu \left[\frac{d\sigma}{dt}\right]^n \qquad (2.)$$

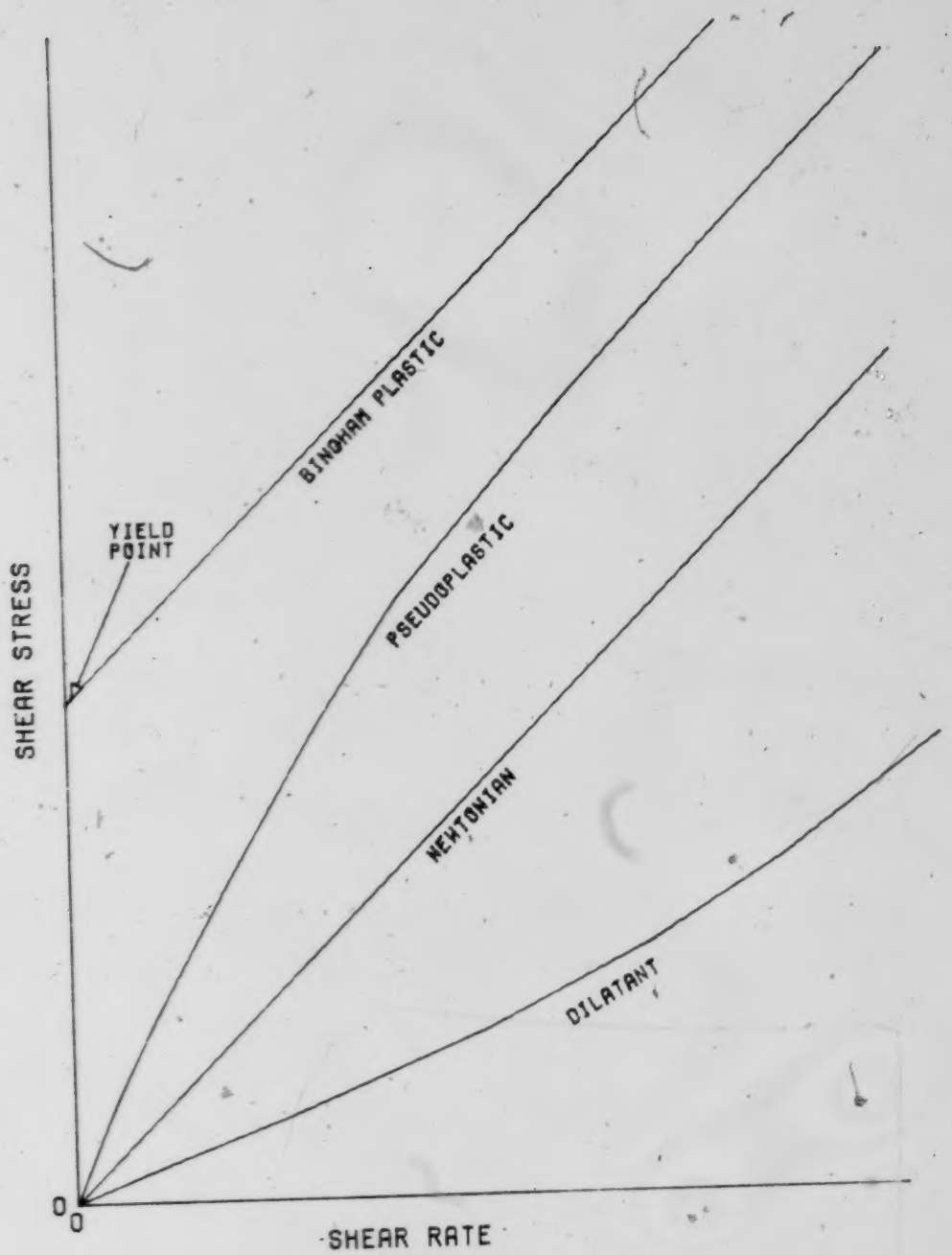


FIGURE 2.1 - A LINEAR PLOT OF TIME INDEPENDENT RHEOLOGY (SHEAR STRESS VS. SHEAR RATE)

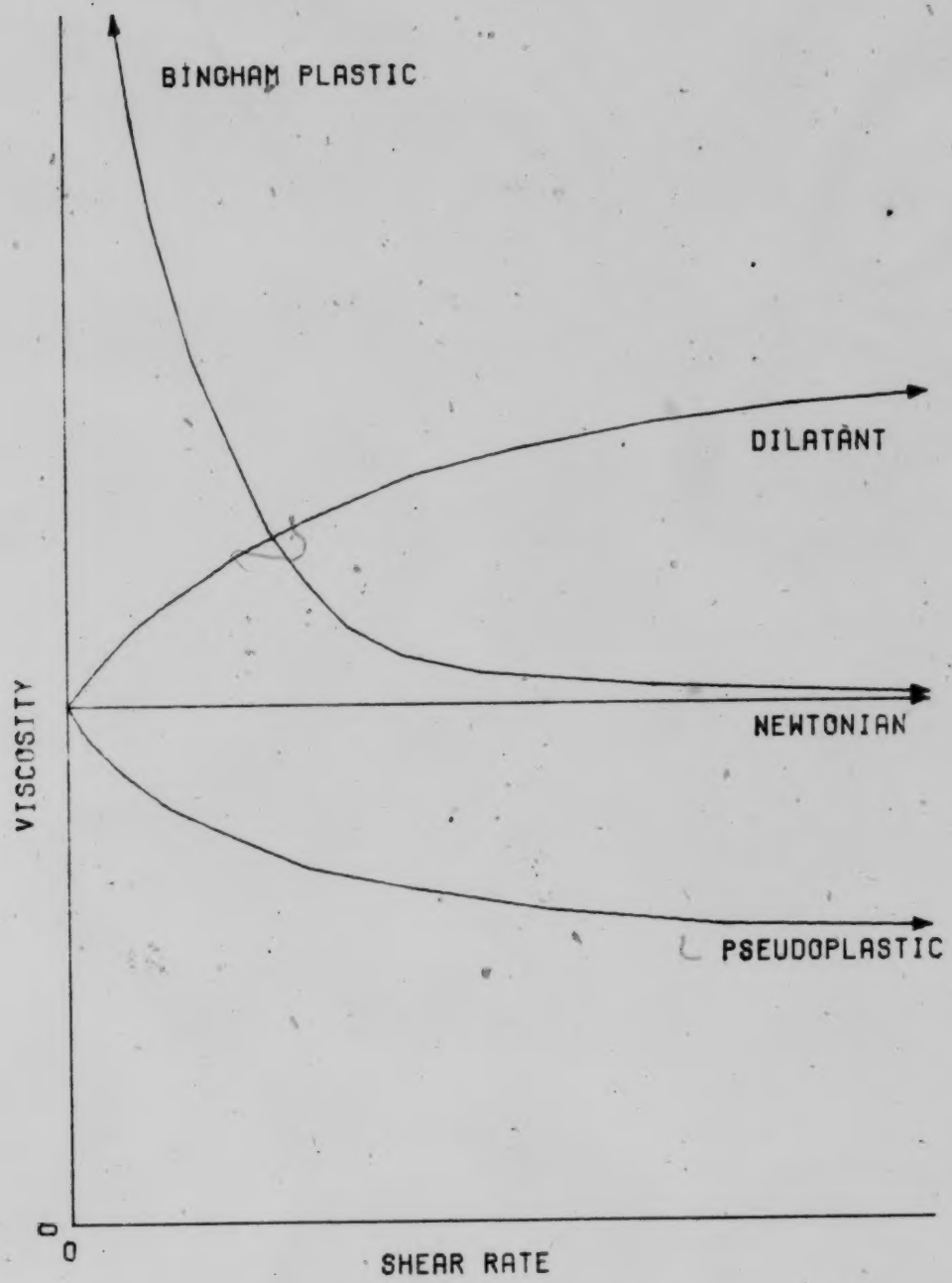
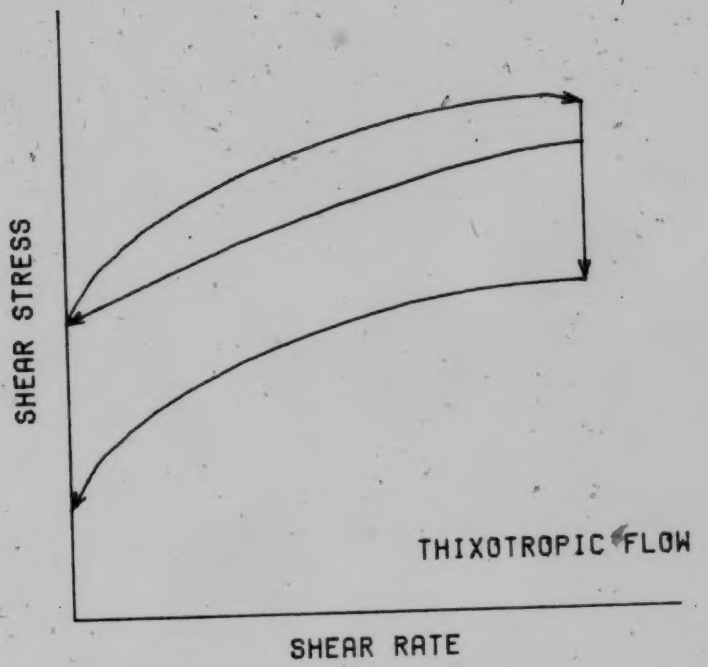


FIGURE 2.2 - A LINEAR PLOT OF TIME INDEPENDENT RHEOLOGY (VISCOSITY VS. SHEAR RATE)



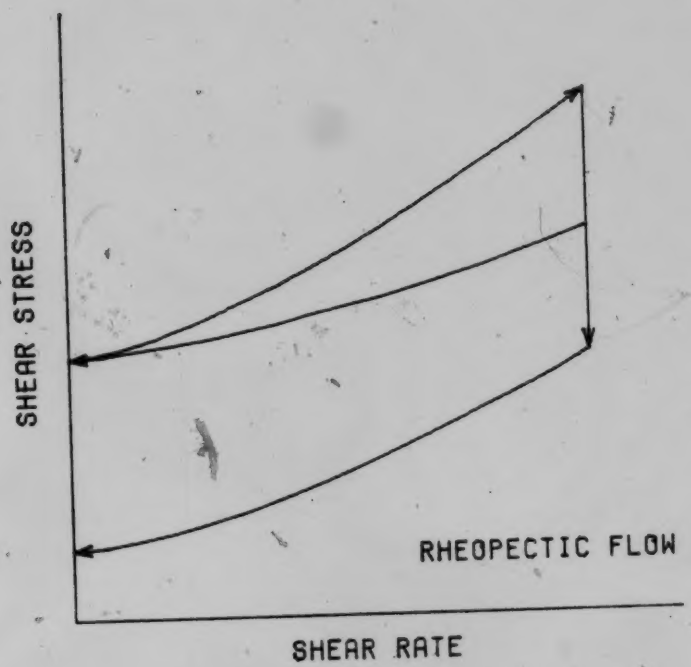


FIGURE 2.3 - A LINEAR PLOT OF TIME DEPENDENT RHEOLOGY

Dilatant

Again the shape of the curve is linear on logarithmic paper but the slope of the graph is greater than 1 (n > 1). A linear plot of shear stress vs. shear rate is curved upward (see Figure 2.1). It can be seen that the shear stress increases proportionately less than the shear rate. A graph of viscosity vs. shear rate shows that the viscosity increases with increasing shear rate (see Figure 2.2).

Thixotropic

Figure 2.3 shows the addition of time dependence on rheologic behaviour. The fluid possesses a structure which breaks down with time as well as shear rate.

$$\tau = \text{Function}(\mu, \sigma, n, t) \qquad (3.)$$

The viscosity decreases with time. The structure may be partially or fully restored with time.

Rheopectic

These materials also exhibit time dependence but now the viscosity increases with time. A graph of shear rate vs. shear stress during rheopectic flow is shown in Figure 2.3.

$$\tau = \text{Function}(\mu, \sigma, n, t) \qquad (4.)$$

Again, as with the case of thixotropic flow, the

structure may break down partially or fully with time (ie. It may not return to the same original shear stress).

III. EMULSION PROPERTIES

A. DEFINITION OF AN EMULSION

Many definitions of emulsions can be quoted but perhaps the most concise is given by Becher [1]

> "An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameters in general, exceed 0.1 μ . Such systems possess a minimal stability, which may be accentuated by such additives as surface-active agents, finely divided solids, etc."

This definition does not include colloidal suspensions but an analogy can be drawn between the rheological behaviour of emulsions and colloidal suspensions.

The physical properties of emulsions which relate to their rheological behaviour are: droplet size distribution, concentration of the two phases, the viscosity of the two phases, electro-viscous effects and the particular emulsifying agents used.

General attempts have been made to correlate the viscosity of the emulsion with the external phase viscosity and the concentration of the two phases but additional factors may need to be considered if a general correlation were to be formed.

B. EMULSION FORMATION PROCESSES

The formation of an emulsion is accomplished by disrupting the interfacial tension between the two immiscible liquids to create droplets of one liquid within the other. As was written by Gopal [2] the resultant emulsion can be thermodynamically unstable and can exist in a metastable state (it can, at some future period in time, separate and go to a lower state hence it is called metastable). The success of the emulsion depends on keeping the system metastable by opposing the droplet coalescence.

Martynov [3] applied surface energy considerations to transition layers between two liquids and concluded that emulsification takes place so as to result in an emulsion in which the liquid possessing a greater value of the ratio:

$$\frac{\text{Compressibility}}{\text{Thermal Expansion}}$$

forms the disperse phase. For example, if the water has a value of the ratio = X, the oil has a value of the ratio = Y and the value of X less than Y, then the oil phase will form the disperse phase.

The addition of an emulsifier in one of the phases could affect the compressibility or thermal expansion of that phase to increase or decrease the above ratio. If that ratio was changed enough to become either larger or smaller than the ratio for the other fluid, conditions could exist to favor the other fluid as the disperse phase. The effects

of the emulsifying agent could then be seen as the effect of the emulsifier on the above ratio. Following the previous example, the effect of the emulsifier can be seen as an effect on the value of the ratio X or Y (depending on the phase the emulsifier is soluble in). If the value of X becomes greater than the value of Y, then the water will form the disperse phase.

Two methods exist to form emulsions. One can start with small nuclei and allow them to grow. This is referred to as the condensation method. The second method involves breaking the interface using physical force and is referred to as the dispersion method.

A simple emulsion can be readily identified as either oil-in-water if the electrical conductivity of the emulsion is high and as water-in-oil if the electrical conductivity is low. An alternative procedure was suggested by Becher. The emulsion was placed on filter paper. If the emulsion spread leaving drops of oil on the surface of the paper, it was considered to be oil-in-water. If the emulsion did not spread, it was considered to be water-in-oil.

A dual emulsion can exist as a continuous phase dispersed within droplets of the dispersed phase. A dual emulsion requires careful examination with a microscope to determine the type. An illustration of a dual emulsion is shown in Figure 3.1 .

Condensation Formation Method

> "If the vapor of any liquid is supersaturated, it tends to deposit on any nuclei that may be present in the system." "The excess material in the supersaturated vapor gets deposited on the nuclei which, as a result, grow in size."
>
> Gopal [4]

The general method of emulsion formation would be to inject a vapour of the first phase at a controlled temperature and pressure into the liquid of the second phase. Small droplets of the dispersed phase would form in the continuous phase. The droplets could then grow in size as more of the vapour is injected.

Dispersion Method

Three main methods exist to create an emulsion on a large scale: mixers, colloid mills and homogenizers.

Mixer

The mixer consists of a tank usually with baffles and a rotating parabolic propeller. The mixing method works best when turbulent flow distributes the liquids both laterally and vertically to all parts of the tank. To produce finer emulsions, two impellers can be used. The lower impeller provides and upward thrust and the upper impeller provides a downward thrust. The mixer produces emulsion droplet sizes usually of the order of 5 μ .

Colloid Mill

The colloid mill emulsifies liquids by shearing the liquid in a narrow gap between a high speed rotor

and a stator surface. The rotor is dynamically balanced and can rotate at speeds of 1000 to 20000 rpm. This produces a finer emulsion of the order of about 2 μ .

Homogenizer

A homogenizer emulsifies the liquids by squeezing them through a small orifice under very high pressure (about 5000 psi). For premixed liquids, a single pass through the homogenizer can produce an emulsion of the range of 1 μ . Finer emulsions are possible by using a series of stages to further break down the droplet size.

C. EMULSIFYING AGENT

The desirable characteristics of an emulsifier as stated by Gopal [5] are as follows:

1. It must reduce the interfacial tension to less than 5 dyne/cm for emulsions formed with agitation.
2. It must absorb quickly around a droplet as a condensed non-adherent film.
3. It must have a specific molecular structure with a polar end attracted to water and a non-polar end attracted to the oil.
4. It must be more soluble in the continuous phase to be readily available for adsorption.
5. It must impart adequate electrokinetic potential.
6. It should be able to emulsify in only small concentrations.

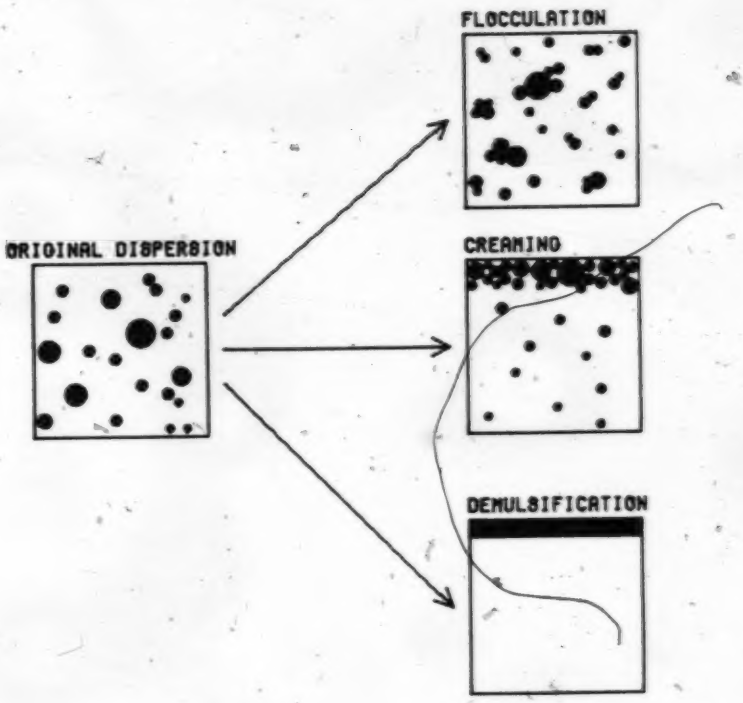


FIGURE 3.2
INSTABILITIES OF EMULSIONS

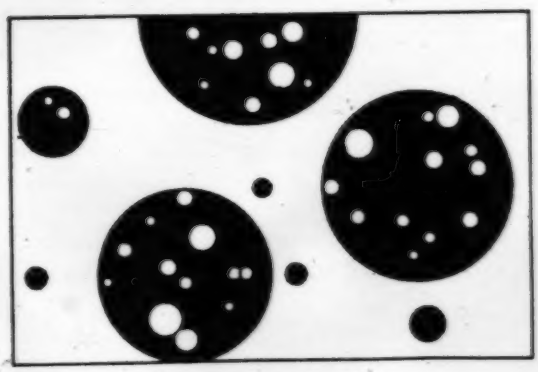


FIGURE 3.1
DUAL EMULSIONS

7. It should be inexpensive, safe to use and non-toxic to handle.

It is very important in emulsion formation to record both the method of emulsification and the emulsifying agents used because both will have an effect on the properties of the emulsion.

McAuliffe [6] reported that asphaltic crude oils that contain natural emulsifiers can be emulsified in water by adding sodium hydroxide. The optimal amount of NaOH to emulsify an oil is found in a narrow range of concentrations. Less than the optimal amount will not emulsify the oil/water mixture and too much can produce a water-in-oil emulsion with a viscosity higher than that of the original oil. Emulsifying agents can be classified in three arbitrary sets:

1. Surface-active materials such as synthetic detergents.
2. Natural occurring materials such as alginates, gums, lipids, sterols, etc.
3. Finely divided solids.

The general method of emulsification reported in the literature involves using synthetic emulsifiers.

D. EMULSION STABILITY

Three stages of destabilization of the original emulsion have been identified as: flocculation, creaming and demulsification (see Figure 3.2).

Jones et al. [7] have shown that highly viscous

interfacial films will slow the rate of coagulation of water droplets in oil which implies a greater stability, however low viscosity interfacial films are not necessarily less stable. It was also determined that the time of oil/water interfacial contact would effect the stability of the emulsion formed for most systems. The authors concluded that laboratory prepared emulsions of freshly contacted oil/water phases do not necessarily give a good representation of field produced emulsions.

Bertness [8] stated that the stability of an emulsion will vary with the composition of the crude oil. The stability in general will increase with the amount of organic colloids and formation fine particles present. The organics and fines solubility would vary with the composition and the temperature of the crude oil.

Jones et al. [9] stated that the time of oil/water interfacial contact affects the stability of the emulsion formed for most systems. Therefore laboratory made emulsions of freshly contacted oil/water phases frequently do not give a good guide to emulsion stability in field operations.

Emulsion stability can be divided into three groups:

1. Unstable
   - changing droplet size with time.
   - phase separation.
2. Low Stability
   - droplet size changes slowly with time.
   - emulsion creams.

3. Stable

- homogeneous emulsion.
- no change in droplet size with time.

Creaming

The phenomena of creaming was given its name from the separation of cream from unhomogenized milk. Basically the separation is not a complete one but a separation into two emulsions, one richer in the disperse phase and the other poorer in the disperse phase. It should be noted that creaming is not a breakdown of the original emulsion but can lead to demulsification over a period of time.

In general, emulsion stability with respect to creaming will be favoured by small droplet radius, small density differences between the continuous and disperse phases and a high viscosity of the continuous phase. Becher [10] also stated that increasing the temperature would increase the rate of flocculation which in turn would increase the rate of creaming. At high temperatures, the interfacial viscosity can become very small which would increase the probability of interfacial film rupture and increase the rate of coalescence.

The phenomena of creaming (neglecting flocculation) was estimated by Becher [11] using Stoke's Law for a high speed centrifuge.

$$V = \left[\frac{d^2 \quad X \quad \omega^2 \quad (\rho_1 - \rho_2)}{18 \quad \mu_e}\right] \qquad (5.)$$

where:

V = rate of creaming of the emulsion (cm/sec)

ω = angular velocity of the centrifuge (1/sec)

X = distance of the sample from the center of rotation (cm)

$\rho_1 - \rho_2$ = density difference of the two phases (gm/ml)

μ_e = viscosity of the emulsion (poise)

d = diameter of the particles in the dispersed phase (cm)

Inversion

An oil-water emulsion is said to have inverted when it changes from a water continuous-oil dispersed phase to an oil continuous-water dispersed phase or vice versa. This is also referred to as an instability.

The simplest theory of inversion given by Ostwald [12] comes from basic geometry. Spheres (in this case representing the emulsion droplets) of equal radii can be most densely packed to occupy about 74% of the available volume. Ostwald proposed that a phase inversion must occur where the concentration of the dispersed phase is greater than 0.74 of the volume. This has subsequently been shown to

be true for only a few systems.

The process of inversion is considered to be a reversible phenomenon (in relation to the increase and decrease of disperse phase concentration) and therefore hysteresis effects must be considered (see Figure 3.3). The reversibility occurs during a change in the disperse phase concentration. It should be noted that the possibility exists that no particular form of the emulsion is favoured in the intermediate range of dispersed phase concentrations and this brings up the possibility that multiple emulsions can exist.

Sherman [13] states that the concentration of the dispersed phase at inversion varies with the emulsifier concentration. Becher [14] showed that the concentration at inversion is both a function of emulsion type and disperse phase concentration.

Wellman and Tartar [15] found that water in benzene emulsions with a sodium soap stabilizer will display an inversion by increasing the temperature with slight agitation and that the system will re-invert if allowed to cool. The inversion temperature was found to be very sensitive to the concentration of the emulsifying agent.

Mao and Marsden [16] observed that an increase in pressure could cause an inversion of an oil-water or water-oil emulsion and that at a temperature, each emulsion has a characteristic shear stress at which the inversion occurs.

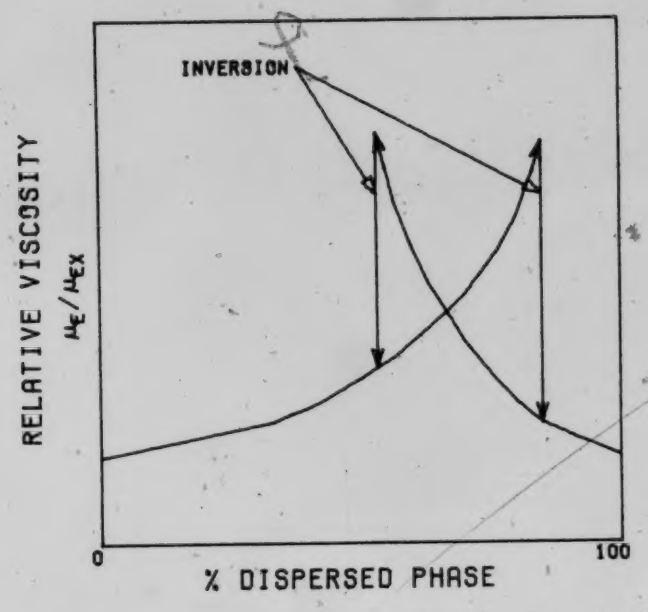


FIGURE 3.3 - HYSTERISIS EFFECTS

Clowes [17] and Bhatnagar [18] investigated the addition of electrolytes to emulsions and pointed out that in the presence of some electrolytes, inversion often occurs and complete demulsification can accompany the inversion.

Demulsification or Coalescence

The breaking of an emulsion may occur by two mechanisms: flocculation and coalescence.

During flocculation the droplets of the disperse phase form aggregates in which the drops do not lose their "identity" (NOT an irreversible process).

Van den Tempel [19] has shown that a "secondary minimum" can occur when two droplets approach each other (for systems with very large droplets). This is thought to be the point at which the process of flocculation could occur.

From the point of view of creaming, these aggregates behave as a single drop, and accelerate the rate of creaming. In sufficiently concentrated emulsions an increase in viscosity is noted.

Although the aggregates are not spherical in shape, the conclusions of Stokes Law would still apply and therefore the aggregates would act as large droplets which would serve to increase the rate of creaming.

Albers and Overbeek [20] studied the relationship between flocculation and the double layer potential of water-in-oil emulsions. They concluded that although zeta potentials exist in these systems, they do not contribute a stabilizing effect. Schulman and Cockbain [21] have shown that these emulsions were stabilized by rigid interfacial films and the interfacial film rigidity may not be related to the zeta potential.

During coalescence, each aggregate combines to form a larger drop. The process is irreversible and leads to complete demulsification.

Coalescence of emulsion droplets which gradually ceases as the droplets approach a limiting size and uniform distribution is termed "limited coalescence" (Wiley [22]).

The distribution of lifetimes of emulsion droplets at the oil-water interface and the mechanism by which emulsion droplets rupture were studied by the authors Cockbain and McRoberts [23] .

Felix and Holder [24] also showed the settling of

dispersions is more rapid with larger droplet size, a larger density difference of the two phases and as the continuous phase viscosity decreases. Using the last effect is is also possible that as the temperature increases the continuous phase viscosity will decrease and the settling of emulsion will be relatively quicker.

Levius and Drommond [25] also investigated the effect of elevated temperature as an artificial breakdown stress to evaluate emulsion stability. The artificial effect of temperature on droplet size distribution and droplet concentration was also shown. Increasing the temperature tends to result in a decrease in droplet size and droplet concentration because of a more rapid settling rate.

Sherman [26] stated that the solubility of the emulsifier in the continuous phase is important for stability of the emulsion at high temperatures for emulsion concentrations up to the inversion point.

E. EMULSION RHEOLOGY

Theoretical Description

The non-Newtonian theory of flow of emulsions is generally explained as flocculation - deflocculation reaction. Sherman [27] explains this process as:

> "The reaction is influenced by both Brownian motion and shear, the importance of the former decreasing as globule size increases and/or rate of shear increases .... If the aggregates (of globules) have a spherical configuration rather than a chain like configuration which is usually adopted, the influence of shear could well be in the form of an exponential in rate of shear rather than a product

in rate of shear with the proportionality factor."

The non-Newtonian flow is described as the reaction of globule aggregates which grow in size at low rates of shear.

Two theories, the "impulse" theory of pseudoplasticity and the theory of kinetics of aggregation are used to describe non-Newtonian flow behaviour but neither theory can be readily applied to experimental data beyond the simple case of monatomic atoms. For a description of the two theories, refer to SHERMAN [28] .

Experimental Studies

McAuliffe [29] states that because of droplet-to-droplet interaction, oil-in-water emulsions containing more than 60% oil exhibit pseudo non-Newtonian flow characteristics. For an oil content of less than 50% the emulsion behaves as a Newtonian fluid. The log-log of the emulsion viscosity was found to vary linearly with the log of the temperature. Alvarado and Marsden [30] also found that oil-in-water emulsions of less than 50% disperse phase concentration were Newtonian at shear rates of 1000 sec^{-1} to 10000 sec^{-1}, and at greater than 50% disperse phase concentration, emulsions were pseudoplastic over the same range of shear rate.

F. EMULSION VISCOSITY CORRELATION

Several authors have attempted to provide correlations to predict emulsion viscosity. It is not the purpose here to identify all existing correlations but to highlight several samples.

Although a universal correlation has not been formed, some relationships can reasonably predict emulsion viscosity using some simplifying assumptions, provided several conditions are met (for a detailed description the reader should refer to the original author quoted). One of the larger constraints on the emulsion correlations involves the condition that the fluid be Newtonian. Even with non-Newtonian emulsions, the correlation could possibly apply at some specific shear rates or failing this the correlation may apply at very high shear rates where the emulsion behaviour is relatively Newtonian.

The effects of the six previously mentioned physical properties on emulsion viscosity are described below.

Viscosity of the continuous (external) phase

Most correlations use a direct proportionality between the emulsion viscosity and the external phase. This can be generally described as:

$$\mu_e = a \quad \mu_{ex} \tag{6.}$$

where:

μ_e = emulsion viscosity (Pa.s)

μ_{ex} = external phase viscosity (Pa.s)

a = proportionality constant
(dimensionless)
(dependent on the other five factors)

It is important to note that the external phase viscosity is not necessarily that of the pure component continuous phase viscosity (since the emulsifier may affect the pure component viscosity).

Concentration of the internal (dispersed) phase

The effect on relative viscosity of the internal phase has been studied by several authors.

The first equation was attributed to Einstein [31] as:

$$\mu_e = \mu_{ex} (1 + 2.5 \Gamma) \qquad (7.)$$

where:

μ_e = emulsion viscosity (Pa.s)

μ_{ex} = external phase viscosity (Pa.s)

Γ = disperse phase concentration (cc/cc)

The correlation was developed from first principles on the basis of solid spheres suspended in a liquid. By assuming that the emulsions are dilute, the effects of inter-particle collisions including the effect of Brownian Motion are

neglected. In this form, the correlation is only valid for dispersed phase concentrations of less than 0.02.

In 1936, Guth and Simha [32] extended the original theory to account for increased hydrodynamic interaction of the individual droplets. The resulting equation is:

$$\mu_e = \mu_{ex} (1 + 2.5 \Gamma + 14.1 \Gamma^2) \qquad (8.)$$

The above empirical equation still assumes that no collision occurs between droplets, aggregation of the droplets does not occur and disregards the effective volume occupied by the droplets. Further investigations suggest that the factor 14.1 should be lower. The correlation is probably only valid for dispersed phase concentrations of less than 0.06.

The correlation by Eilers [33] is of particular interest because it was derived using emulsions of water-in-paraffin oil or bitumen. The equation is given as:

$$\mu_e = \mu_{ex} (1 + 2.5 \Gamma + 4.94 \Gamma^2 + 8.78 \Gamma^3) \qquad (9.)$$

Oliver and Ward [34] developed the general form of the previous equations which can be expressed as:

$$\mu_e = \mu_{ex} \left[\frac{1}{1 - k\Gamma} \right] \qquad (10.)$$

where k is an empirical constant = 2.5 in general. For the Oliver-Ward Model using a rotation cylinder viscometer the constant k was found to be approximately 2.56. This correlation only applies for the disperse phase concentration range of less than 0.2.

Vand [35] pointed out the importance of collisions between spheres and the creation of temporary "doublets", "triplets" and higher orders, up to the point where nearly all spheres can be combined into closely packed aggregates of droplets. At higher concentrations the liquid "frozen" into these aggregates was shown to increase the effective concentration during shear by the factor 1.35 (called h - the hydrodynamic interaction constant). The aggregate may be regarded as immobilizing all liquid situated in its "pore space". The immobilized liquid has no sharp boundary but as Vand points out, the approximate shape will follow the outer outline. Although the droplets are not strictly spherical as the assumption requires, a small amount of ellipticity does not apppreciably alter the factor h. At low concentrations Vand uses the assumption that a doublet behaves as a spheriod of length 2a and minimum radius a so that the volume is calculated to be $10\pi a^3/3$ as opposed to the

individual drop volumes totalling a volume of $8\pi a^3/3$ (see Figure 3.4). The effective volume of the dispersed phase increases by a factor of 5/4. Therefore, when the effective dispersed phase concentration is 0.05, the effective concentration is 0.06 and at a concentration of 0.075, the effective concentration would be 0.094. This crude estimate serves to show that even at low concentrations, the effective concentration can be appreciably higher than the measured concentration.

A general form where high rates of shear occur in concentrated emulsions uses a "free" volume of the continuous or dispersed phase as:

$$\propto 1 - h\Gamma$$

It should be noted that at concentration 0.7405 of the dispersed phase, a singularity exists. This is described as the point at which the suspension becomes closely and rigidly packed (the inversion point as stated by Sherman).

The general equations for the emulsion viscosity correlation quoted by Sherman take the form of:

$$\mu_e = \mu_{ex} \left[1 + \frac{a\Gamma}{1 - h\Gamma} \right] \qquad (11.)$$

or:

$$\mu_e = \mu_{ex} \exp \{ (a\Gamma / (1 - h\Gamma) \} \qquad (12.)$$

where a is fitted to the experimental data and is approximately 2.5.

An empirical correlation offered in the literature is given by Arrhenius [36] as:

$$\mu_{e_m} = (\mu_{ex})^{1-\Gamma} (\mu_i)^{\Gamma} \qquad (13.)$$

Where μ_{e_m} = the geometric mean viscosity.

Richardson [37] used the semi empirical equation:

$$\mu_e = \mu_{ex} \exp\{ K\Gamma \} \qquad (14.)$$

or:

$$\mu_{rel} = \exp\{ K\Gamma \} \qquad (15.)$$

where $6 \leq K \leq 7$ for oil-in-water emulsions and $3 \leq K \leq 4$ for water-in-oil emulsions.

$$\mu_{rel} = \frac{\mu_e}{\mu_{ex}} \qquad (16.)$$

The equation was based on the assumption that the rate of increase in viscous resistance by crowding of the droplets would increase in proportion to the increase in volume of droplets present.

Viscosity of the Dispersed (Internal) Phase

A refinement of the original Einstein equation to account for the effect of internal phase viscosity was conducted by Taylor [38]. A special set of boundary conditions were used to refine the Einstein case to include some effects of liquid spheres interspersed in a second

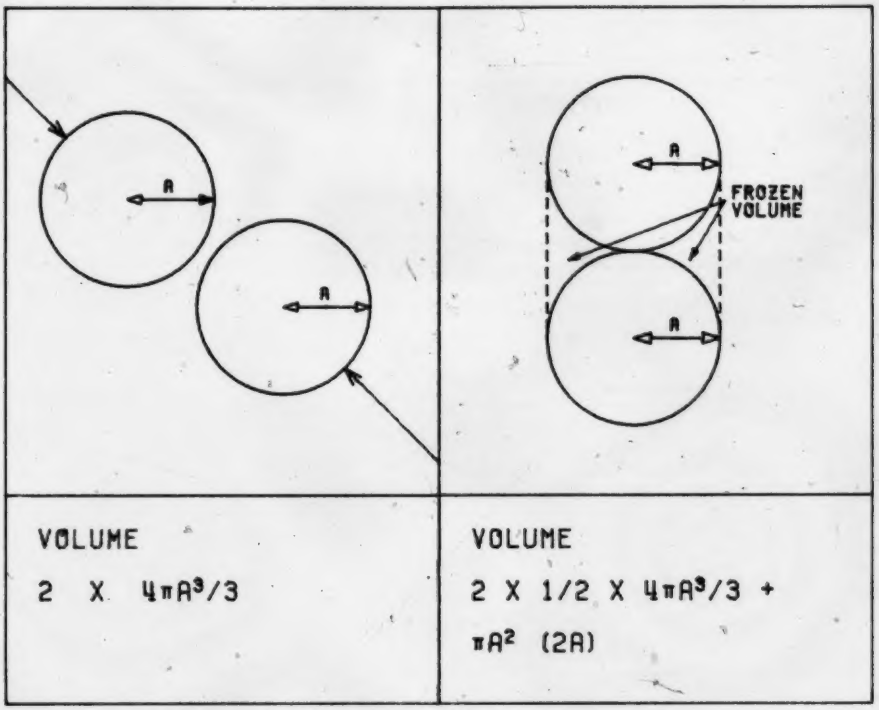


FIGURE 3.4
FLOCCULATION AND
EFFECTIVE DISPERSED PHASE VOLUME

liquid phase. In addition to the assumption of a very dilute solution, it was assumed that:

1. the liquid droplets remain spherical.
2. no slippage occurs at the surface of the droplet.
3. the tangential stress is continuous at the droplet surface so that the film merely transmits the tangential stress from one fluid to another.

The equation is given as:

$$\mu_e = \mu_{ex} \left[1 + 2.5\Gamma \frac{\mu_{ex} + (2\mu_i/5)}{\mu_{ex} + \mu_i} \right] \quad (17.)$$

The correlation is probably only valid for disperse phase concentration range of less than 0.03. Where μ_i goes to infinity it can be seen that the above equation will become the Einstein equation.

Note, as μ_i becomes large it implies "solid" emulsion droplets by virtue of the small deformation of the droplets.

Droplet Size Distribution

Leviton and Leighton [39] observed the viscosity of dilute emulsions did not change when droplet mean diameter was varied from 0.7 micron to 3.0 micron.

Richardson [40] observed concentrated emulsions where the concentration of the dispersed phase was 0.75 and found that the viscosity at constant shear (for long times) was directly proportional to the inverse of the mean droplet diameter.

Gopal [41] proposed:

$$\mu_e = \mu_{ex} \left[1 + \frac{2.5\Gamma \{\mu_i + \frac{2\mu_{ex}}{5} + \frac{2\mu_{ex}\mu_i}{S_c r}\}}{\mu_{ex} + \mu_i} \right] \quad (18.)$$

Where S_c is the slippage coefficient between globules and

continuous phase. This only applies to very dilute emulsions. At high shear rates, if the droplets in an emulsion are completely deflocculated so that all structure is destroyed and all droplets are equidistant then the equation by Sherman [42] applies.

$$a_m = 2 r \left[\left(\frac{\Gamma_{max}}{\Gamma} \right)^{1/3} - 1 \right] \qquad (19.)$$

where:

a_m = mean distance between emulsion droplets

r = mean radius of the emulsion droplets

Γ_{max} = maximum dispersed phase concentration (before emulsion inverts)

Γ = volume fraction of dispered phase

The equation of course depends upon the homogeneity of the system and will not apply where a * less than 1 micron (because particle charges and other effects become very important at less than 1 micron). Sherman found (in some cases) that a higher homogenization pressure was required to produce emulsion droplets of equal size for a higher dispersed phase concentration. A constant rigid emulsion formation technique may not produce the same size emulsion droplets over all concentration ranges.

Emulsifier

As previously mentioned, the emulsifier must be taken into account when the viscosity of the external phase is

measured (assuming the emulsifier is soluble in the external phase).

Sherman [43] showed that an identical oil and water, in the same amounts, with a different emulsifier, produced different relative viscosities.

The summary of emulsifier effects stated by Becher [44] supports the contention that emulsion viscosity is dependent on the nature of the emulsifier. To a lesser extent the emulsion viscosity is dependent on emulsifier concentration.

Electroviscous Effects

Smoluchowski [45] is credited with the first investigation of electroviscous effects on emulsions. Smoluchowski studied charged and uncharged lyophobic colloids and found that an electrically charged system exhibited a viscosity greater than an uncharged system. Taking the effect into account, the Einstein equation was modified to:

$$\mu_e = \mu_{ex} \left[1 + 2.5\,\Gamma \left[1 + \frac{4}{d^2\ \kappa\ \mu_{ex}} \left(\frac{\epsilon\ \xi}{2\ \pi} \right)^2 \right] \right] \quad (20.)$$

d = diameter of the particle or droplet

κ = specific conductivity of the suspension

ϵ = dielectric constant of the medium

ξ = electrokinetic potential of the charged particles (zeta potential)

The assumption is made that the thickness of the the double

charge layer is very small compared to the droplet size.

G. VISCOMETERS

The four principal types of viscometers used in measuring rheological properties are: capillary, co axial-cylinder, cone-plate and rolling or falling ball viscometers.

Capillary

The capillary viscometer can measure both Newtonian and non-Newtonian behaviour of fluids. The principal corrections required are for entrance effects, kinetic energy imparted to the sample, wall effects and turbulent flow. Since the sample being measured is constantly being replaced it is not a good method for measuring the time change in shear rate vs. shear stress (thixotropic or rheopectic properties). In measuring an emulsion viscosity the disperse phase tends to migrate axially along the viscometer tube. This results in fluctuations of concentration of the disperse phase, which can lead to erroneous results. There is also a possibility where the emulsion droplet size becomes large that the assumption of infinitesimally thin shearing layers may not be valid and therefore measurement with a capillary viscometer may be misleading. Capillary viscometers are particularly suited to measure very high shear rates.

Co-Axial Cylinder and Cone-Plate

The coaxial cylinder and cone-plate viscometers can also measure both Newtonian and non-Newtonian behaviour of

fluids. The principal corrections are for end effects and turbulent flow in the end region. Care must be taken to insure the annular gap is filled with sample fluid and that the fluid does not overflow the gap when an angular torque is applied (particularly at high shear rates). At high shear rates, heating due to friction becomes important and this results in poor temperature control. The end effect becomes even more significant if turbulent flow at the end occurs simultaneously. For Newtonian viscosities greater than 1 poise, the correction is a constant, but below 1 poise the end effect increases. The coaxial cylinder viscometer can only be used to study highly viscous emulsions when the annular gap is large. This introduces an error into the principal assumption of a uniform shear across the gap. At higher rotational speeds, the emulsion droplet size distribution may change because of the possible effect of breaking larger emulsion droplets by shear forces.

Rolling Ball

The rolling ball viscometer is suited only to measurements of Newtonian fluids. Shear stress for the falling ball cannot be estimated. The principal corrections are for end effects and wall effects. Only a small range of emulsions can be used in the viscometer because of the dependence on electric timing of the rolling ball.

IV. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. CRUDE OILS

Two types of crude oils were used in this study. The two oils were: Epping Crude Oil and Cold Lake Crude Oil.

Epping Crude Oil

The crude has an API gravity of about 11.8° and a viscosity of about 50000 cp at 21°C (1.0 sec^{-1}). The crude oil was produced in May, 1976 and dried in February, 1978. The long period of storage changed some of its properties (specifically, aging may increase the viscosity by slow oxidation of the crude oil). The original viscosity measured was 1120 cp at 0.89 sec^{-1} and 40°C for the dried crude oil (estimated by extrapolating the viscosity to 21°C, the viscosity would be 4760 cp).

Cold Lake Crude

This crude was sampled from the downstream side of the separator (treated and dewatered) on April 1981.

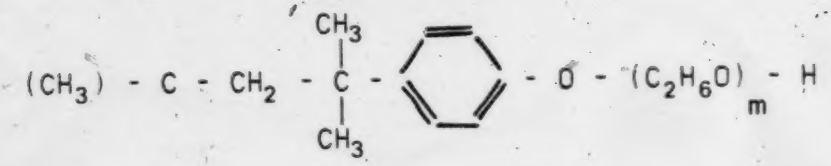
The crude has an API gravity of 11.1° and a viscosity of about 40000 cp at 21°C (at 1.0 sec^{-1}).

B. EMULSIFIER

The oil-water emulsions used in this study were formed using a variable speed blender and stabilized with Triton X-100 surfactant.

The surfactant Triton X-100 is a nonionic water soluble molecule (iso-octyl pheoxypolyethoxy ethanol) with 9 to 10

ethylene oxide units. Its molecular weight is 628. Triton X-100 has the formula:



where $8 \leq m \leq 10$. Triton X-100 was supplied by Union Carbide.

Triton X-100 has a density of 1.065 gm/cc and a viscosity of 240 cp at 25°C. Its surface tension at 0.5% (by volume concentration) is about 31 dyne/cm.

C. EMULSIFICATION METHOD

The emulsion was prepared in approximately 1 litre batches. Exactly 5ml of surfactant constituting 0.5% by volume of the emulsion prepared in one batch, was added to 90.0 ml oil and 1000ml distilled water to make an 8.2% oil-in-water emulsion. The surfactant concentration was in excess of the minimum amount required to obtain a stable emulsion.

A variable speed Gifford-Wood Homogenizer (variable speed mixer model 1-LV ; 0 - 7500 RPM) was used to mix the oil-water emulsion. A photograph of this equipment is shown in Plate B.1. It should be noted that the mixer used is not a true homogenizer as described in Chapter III, but is in reality a turbine mixer.

The emulsions were mixed first at low speed for 8

minutes. The mixer was then stopped for 4 minutes to allow any trapped air to rise out of the emulsion. The emulsion was then mixed at high speed for a further 7 minutes.

Oil-in-water emulsions were formed by simple simultaneous mixing in a container at room temperature. Water-in-oil emulsions were prepared by first preheating the oil to about 60°C and then gradually adding water to the oil while mixing at low speed. The resulting oil-in-water emulsions were formed at about 30°C (some heating of the sample during mixing occurred due to friction effects) and the water-in-oil emulsions were formed at about 60°C.

In calculating the emulsion quality, the surfactant was assumed to be part of the aqueous phase.

The emulsion quality was confirmed by distillation and the results were in excellent agreement with the original composition.

As a further test of emulsion consistency of formation, emulsion batches of 70% oil-in-water were diluted to 20, 12 and 6% oil-in-water (dilution with a solution of 0.5% Triton X-100 in distilled water) and their viscosities compared to the original batches of oil-in-water emulsions. It was found that the diluted emulsions exhibit the same viscosities as the original emulsions to within the accuracy of the measuring technique. This is true providing the dilution is completed such that the resulting emulsion sample has the same concentration of surfactant as the original (in this case 0.5% by volume).

Emulsion Properties

Emulsion Stability

Before studying the rheologic properties of the emulsion, a test of emulsion stability was conducted. The parameters of surfactant type, concentration of surfactant, mixing temperature and mixing time were varied to determine their empirical relation with emulsion stability.

The emulsions used in this study exhibited no phase separation when stored over a period of weeks in an airtight container. The emulsion was qualitatively determined to be of low stability. The emulsion did tend to cream, but was easily redispersed upon stirring. During a qualitative observation of the emulsions, it was noted that a greater dispersed phase concentration tended to display a faster rate of creaming.

Density

Emulsion density was measured using an Anton Paar Density Meter DMA 512 and DMA 60 at constant pressure over a range of temperatures. The equipment is shown in Plate B.3. The densities were recorded for the distilled water, crude oil and the corresponding emulsions over a range of temperatures of 25°C to 140°C.

Emulsion Droplet Distribution

An emulsion sample was diluted and put on a microscope slide (a photograph of the equipment used is show in Plate B.2). The particular oil-in-water emulsions were diluted with a solution of 1% Triton X-100 in distilled water and the water-in-oil emulsions were diluted with toluene. The range of droplet sizes could then be directly measured from the photographs.

D. VISCOSITY MEASUREMENT

The viscosity was measured with a Haake Rotovisco RV 3 viscometer, a Brookfield Synchrolectric viscometer and a Weissenberg Rheogoniometer Model R18. The Haake viscometer uses a concentric cylinder system, the Brookfield viscometer uses a series of spindles and the Rheogoniometer uses a cone and plate apparatus to measure apparent viscosity.

Before taking the measurements, all viscometers were calibrated with a laboratory standard oil (CanAm 1000 Fluid, Lot 7880 - 950 cp @25°). All viscometers were thoroughly cleaned between measurement of samples. Shear rates used in the calculations of emulsion viscosity were as reported in each manual (given with each viscometer).

A check on the viscosity at room temperature was performed using the Brookfield viscometer. In the case of the Brookfield viscometer, the viscosity reading would fluctuate ±50% of the shear stress value when measuring water-in-oil emulsions of very large concentrations. In most

cases the viscosity reading on the Brookfield viscometer tended to fluctuate.

Haake Viscometer

The Haake viscometer uses an EF type measuring head which consists of a stainless steel cylinder that rotates within another stainless steel cylinder (photograph shown in Plate B.4). A photograph of the Haake apparatus is shown in Plate B.5. Slits have been cut in the outer cylinder to allow the sample to circulate in the viscometer. Because the entire gaps between the two cylinders are filled with sample fluid and the outer cylinder has slits cut into it, the calculation of shear rate between the cylinders becomes complex due to the complex geometery. The equations for the case of simple geometry are:

1. for shear rate at the outer wall

$$\left[\frac{d\sigma}{dt}\right]_{max} = \frac{2\omega}{r_1^2(r_2^{-2} - r_1^{-2})} \qquad (21.)$$

2. for shear rate at the inner wall

$$\left[\frac{d\sigma}{dt}\right]_{min} = \frac{2\omega}{r_2^2(r_2^{-2} - r_1^{-2})} \qquad (22.)$$

where:

ω = angular speed (radian/sec)

r_1 = inner cylinder radius (cm)

r_2 = outer cylinder radius (cm)

This means that for the viscometer, the shear rate at 1 rpm would be 2.2 sec^{-1}. This can be compared to the quoted value of 2.34 sec^{-1} in the manual.

A test sample of about 500ml was placed in the constant temperature vessel and the temperature was adjusted to the desired value. The sample was left for 2 hours while the constant temperature bath circulated fluid through the constant temperature vessel jacket. During that time the viscometer was held at a low constant speed to aid in mixing the sample and to obtain a uniform fluid.

The sample was then ready for the rheological measurements. The rotational speed was set to a range of fixed speeds (which were varied from low shear rate to high shear rate) and the corresponding torque values were recorded on a Hewlett Packard X-Y recorder. After varying the shear rate through a series of fixed values the equipment was stopped and the procedure was repeated to insure repeatability.

The Haake viscometer was used to evaluate the rheology of water-in-oil emulsions with changing temperature and concentration of water.

Weissenberg Rheogoniometer

For the cone and plate apparatus, the equation used to calculate the shear rate is:

$$\frac{d\sigma}{dt} = \frac{\text{angular velocity}}{\tan\beta} = \frac{30 \quad (RPM)}{\beta} \qquad (23.)$$

where:

β is in radians (cone angle=0.531°)

angular velocity is in radians/second

A photograph of the Weissenberg apparatus is shown in Plate B.6.

A test sample of about 50 ml was placed in the bottom cone of the cone and plate apparatus. It should be noted that about 2ml of the sample is held in the gap between the cone and plate at one time. The remainder is held in the special reservoir attachment surrounding the cone and plate. A photograph of the cone and plate with reservoir attachment is shown in Plate B.7. The gap of the cone and plate was adjusted to the prescribed distance stated in the viscometer manual (in this case 25 microns). The measurement of gap distance was accurately measured using a differential transducer. The sample and the cone and plate apparatus were left for about 1 hour to insure that the temperature of the fluid would be room temperature (70°F,21°C).

As with the Haake viscometer, the cone and plate apparatus was set to a range of fixed speeds (shear rates) and the corresponding torque values (shear stress) were measured on a chart recorder. Again the sequence of rheological measurements were made from low to high shear rate with each sample. The measurements taken were found to be highly reproducible.

By keeping the speed fixed, the additional effect of time dependent viscosity could be measured (if it was

significant).

The Weissenberg viscometer was used to determine shear stress over a large range of shear rates (but only at room temperature).

Turbulence in Cone and Plate Viscometery

Using the calculation method of Cheng [46], the effects of turbulence would be predicted at about 4300 sec^{-1}. The effects of turbulence would increase the apparent value of the torque above the true value for the fluid because of the secondary flow. In all runs, the shear rate was kept to below 2000 sec^{-1} to insure laminar flow.

V. RESULTS AND DISCUSSION

A. EMULSION DENSITIES

The density of Epping Crude Oil and its oil-in-water and water-in-oil emulsions as a function of temperature is shown in Appendix A, Figures A.1 and A.2. The density of Cold Lake and its emulsions are shown in Appendix A, Figures A.3 and A.4.

An example of the density relation of Epping oil-in-water with temperature is shown in Figure 5.1 (this is a copy of Figure A.1 from Appendix A). The graph shows the typical relation where the density curves downward as temperature increases. This is in contrast to the generally quoted linear decline of density vs. temperature. Examples of the linear decline of density vs. temperature are shown by Rojas ETAL [47] and Hallam [48]. A comparison of the measured values of the density of water and the values quoted in the Chemical Engineers Handbook [49] are shown in Figure A.5. It can be seen that both sets of values show the non-linear nature of the graph of density vs. temperature. It is also apparent that observed data is in agreement with the published data. Previous results quoted in the literature were generally measured using the pcynometer or the hydrometer.

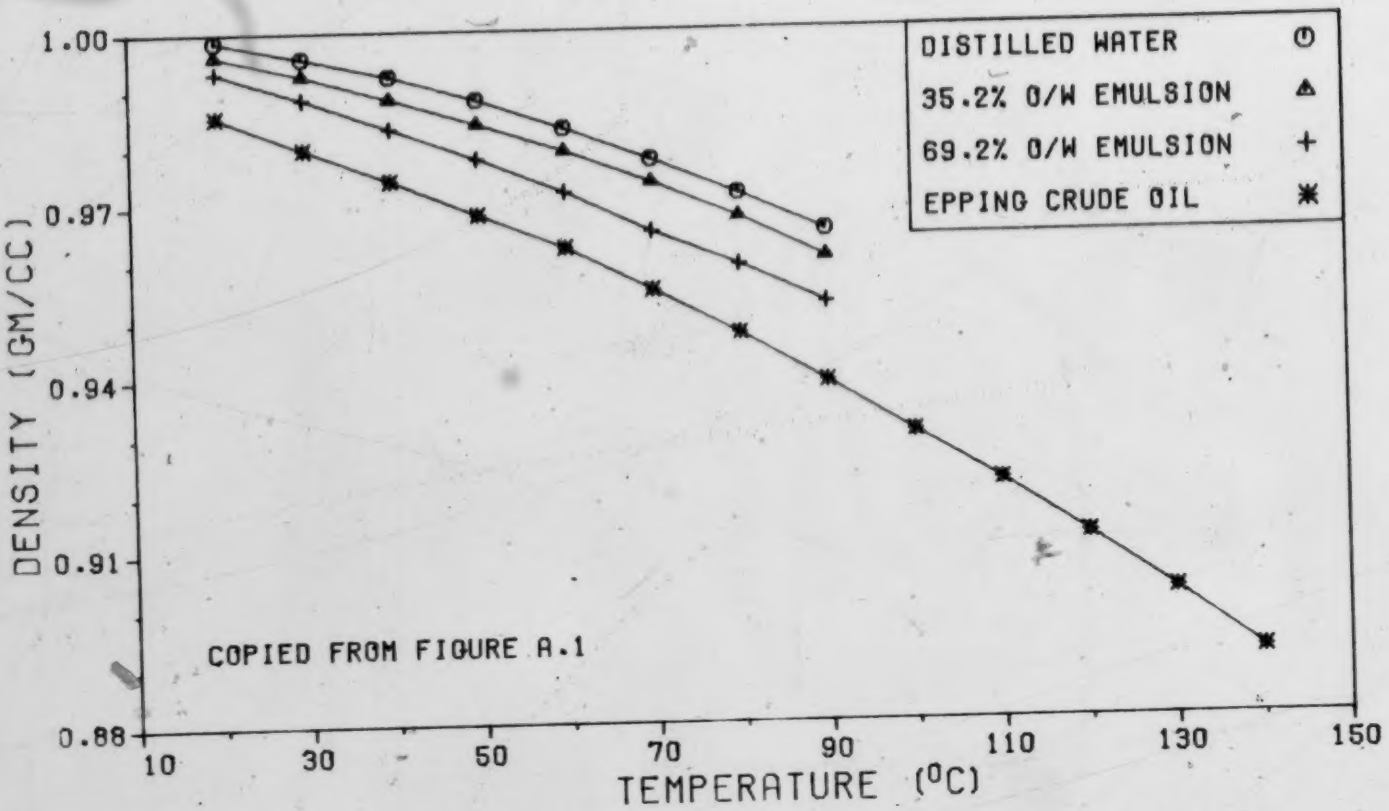


FIGURE 5.1 - O/W EMULSION DENSITIES
EPPING CRUDE OIL

B. EMULSION DROPLET SIZE

PARKINSON ETAL [50] has shown that the smaller droplets (of less than 1 micron) have a greater effect in increasing the emulsion viscosity than the larger droplets even though the smaller droplets occupy much less of the disperse phase volume.

It can be seen from the emulsion photographs found in Appendix C, in particular Plates C.16 and C.18, that the oil-in-water emulsions are dual emulsions. The oil-in-water emulsions exist as water droplets of less than 10 microns within oil droplets of between 2 to 100 microns, which in turn exist as a disperse phase within the continuous water phase. The water-in-oil emulsions appear to exist primarily as water droplets within the continuous oil phase.

From the comparison of the emulsion pictures in Appendix C, for example Plates C.4 and C.5, (immediately after formation and after a period of 12 days), it is apparent that the droplet size increases very slowly with time. This implies a low stability of the emulsion (see the definition of stability in Chapter III).

If one observes any single oil-in-water emulsion, it can be seen that the droplet distribution is very broad (approximately 2 to 200 microns) for both the Epping Crude and the Cold Lake Crude Oil. For water-in-oil emulsions, the droplet distribution appears to be narrower with a droplet size ranging from 1 to 20 microns.

Comparing the droplet sizes of each of the range of

disperse phase concentrations, it can be seen that the droplet size distribution does not vary significantly with disperse phase concentration. For example, the 14.9% oil-in-water Cold Lake Emulsion shown in Figure C.1 is very similar to the 59.7% oil-in-water Cold Lake Emulsion shown in Plate C.7. Also, the 18.1% water-in-oil Cold Lake Emulsion shown in Plate C.9 is of similar droplet size to the 38.3% water-in-oil Cold Lake Emulsion shown in Plate C.13. In contrast to this, a large change in droplet sizes can be seen with the comparison of Cold Lake and Epping Crude Oils (compare Plates C.2 with Plate C.18). This is in contrast to that reported by Mao [51]. Mao found that the average emulsion droplet size increased with increasing disperse phase concentration. Sherman has also made the general statement that the droplet size need not remain constant for a constant oil, water and emulsifier system. It is possible that a longer mixing time may be required to produce a more uniform droplet size distribution.

In general, the literature reports investigations of single emulsions and it should be emphasized that the dual emulsions found here may exhibit different properties.

C. OIL AND WATER PHASE RHEOLOGY

Viscosities for the "pure" components of the emulsions were measured and are shown in Figures A.7 and A.13 for the dried Epping and dried Cold Lake Oils respectively. Viscosities of the water phase (distilled water with 0.5% by

volume Triton X-100) are shown on the figures of oil-in-water emulsions as 0% oil-in-water (Figures A.12 and A.18 for Epping and Cold Lake Emulsions respectively).

An example of the viscosity vs. shear rate rheology of Epping Crude Oil is shown in Figure 5.2 (this is a copy of Figure A.7 of the appendix). As can be seen, the graph of Epping Crude Oil viscosity vs. shear rate shows a slight decrease in viscosity with increasing temperature (over the temperature range of 40 to 80°C). The decrease in viscosity with shear rate is indicative of a pseudoplastic fluid. For the range of 20 to 40°C, the viscosity increases slightly with shear rate. This indicates a fluid which is dilatant (but only slightly so since the curvature is minor). The graph of the Cold Lake Oil viscosity vs. shear rate (see Figure A.13 of the appendix) is relatively flat over the range of temperatures from 20 to 100°C which indicates a fluid which is relatively Newtonian.

The water phase (or solution of 0.5% Triton X-100 with distilled water) exhibits a Newtonian behaviour at room temperature ie. the graph of viscosity vs. shear rate is a constant.

D. OIL-IN-WATER EMULSION RHEOLOGY

Figures A.12 and A.18 show the respective rheological behaviour of Epping and Cold Lake oil-in-water emulsions. An example of the viscosity vs. shear rate rheology of Epping Oil-in-Water Emulsions is shown in Figure 5.3. It can be

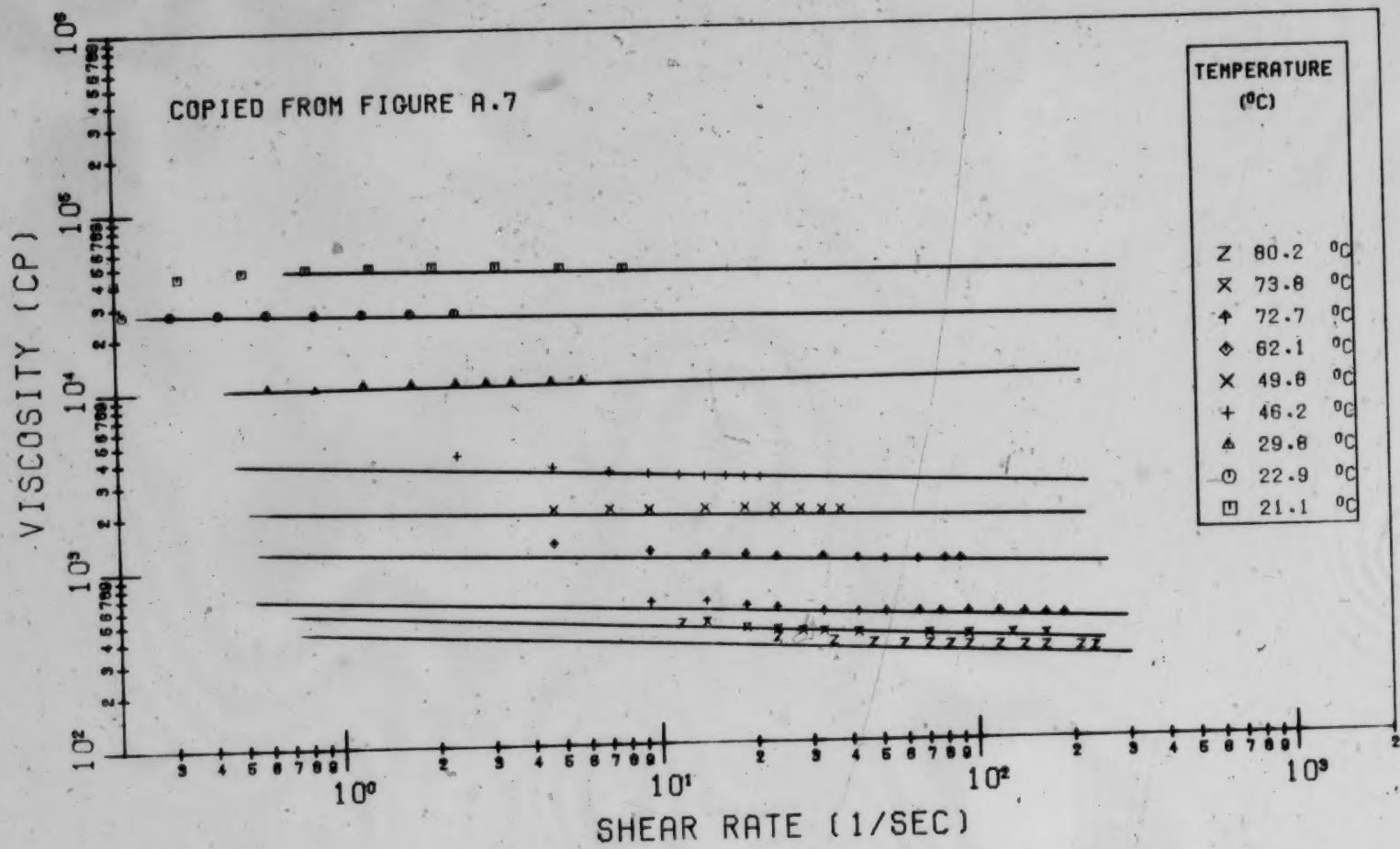


FIGURE 5.2 - RHEOLOGY OF DRIED CRUDE OIL EPPING CRUDE OIL

seen that the emulsion with a disperse phase concentration of less than 20% has a relatively constant viscosity over a range of shear rates. The Cold Lake Oil-in-Water Emulsion is similar to the Epping Oil-in-Water Emulsion. Both emulsions are then said to be Newtonian for disperse phase concentrations of less than 20%. At higher disperse phase concentrations, the general tendency of both emulsions to decrease in viscosity with increasing shear rate is described as being pseudoplastic. Both emulsions displayed a 0 shear stress at 0 shear rate (to within the accuracy of the particular viscometer) which indicates the absence of any gel strength (such as in a Bingham Fluid).

It is interesting to note that although the oils are relatively similar, the viscosity of the oil-in-water emulsions at 70% disperse phase concentration are 600 cp and 200 cp (at 1 sec^{-1}) respectively. This implies that although the oils appear similar in some of the physical properties measured, differences in other properties must exist to account for the discrepancy. Differences may be possible in electroviscous or surface effects and the chemical makeup of the crude oils.

Newtonian Behavior

It can be seen from Figure 5.3 (or Figures A.12 and A.18), that for low concentrations of the disperse phase, the viscosity does not vary significantly with shear rate. This is indicative of a Newtonian type fluid.

The Newtonian effects can generally be attributed to

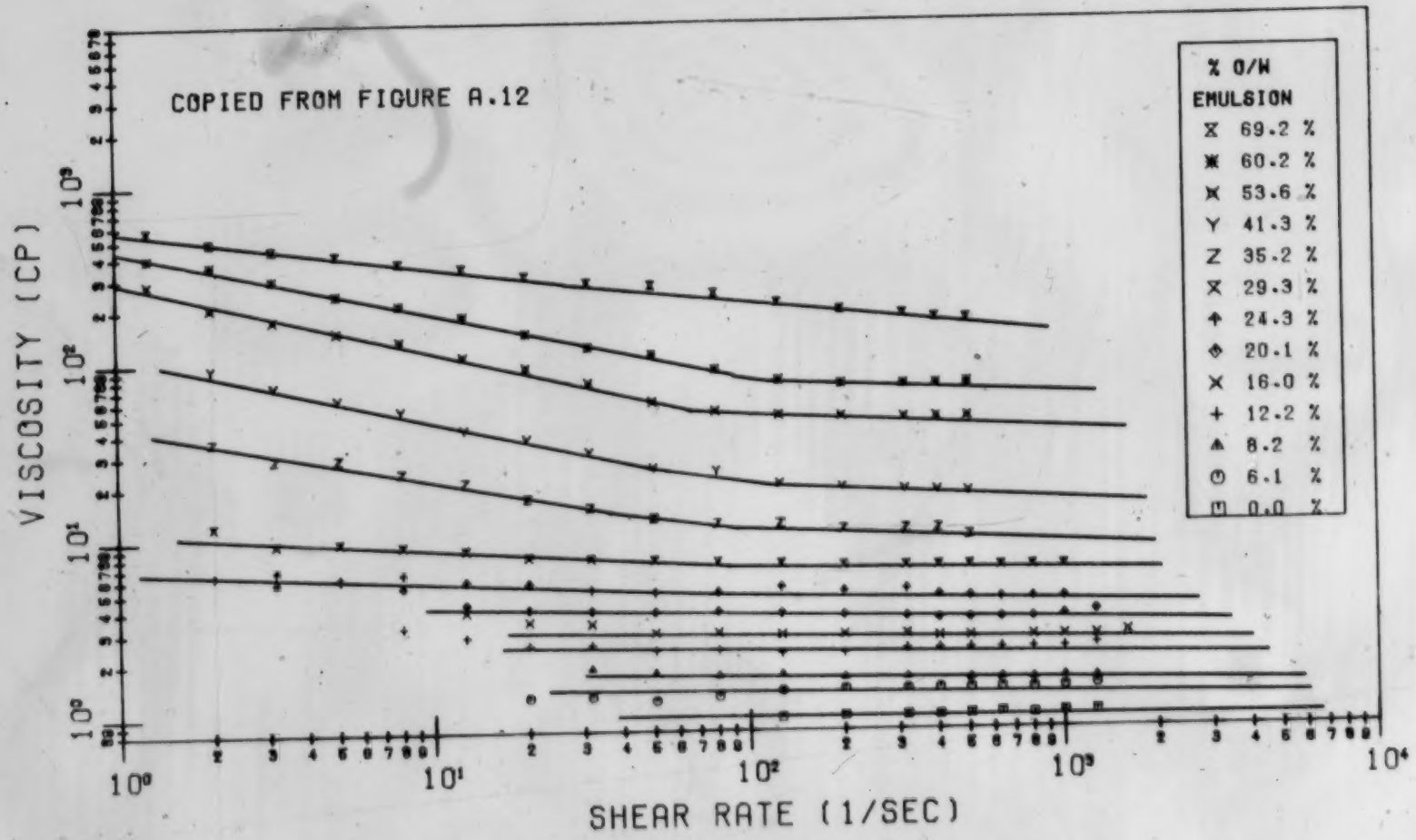


FIGURE 5.3 - RHEOLOGY OF EPPING CRUDE O/W EMULSIONS AT ROOM TEMPERATURE

relatively large interdroplet distances. The large interdroplet distances imply that fewer droplet interactions occur and therefore the viscosity will not be affected to the same degree as with the concentrated emulsions.

It can be seen that at high shear rates of 1000 sec^{-1} and greater, even the non-Newtonian emulsions of up to 50% disperse phase become relatively Newtonian in behaviour. Alvarado and Marsden [52] have also found that for emulsions of up to 50% disperse phase concentration, the behaviour is relatively Newtonian at shear rates of 1000 to 10000 sec^{-1}.

Pseudoplastic Behavior

It can also be seen from Figure 5.3 (or Figures A.12 and A.18 of the appendix), that for disperse phase concentrations of 20 to 70%, the viscosity decreases with increasing shear rate. The behaviour of the 70% oil-in-water emulsion however shows a relatively smaller variation of viscosity with shear rate. The general behaviour of these emulsions would be classified as pseudoplastic.

The pseudoplastic behaviour of the larger disperse phase concentrations may be partially attributed to a flocculation-deflocculation reaction related to shear stress as reported by Sherman [53]. The growth of droplet aggregates could occur at low rates of shear and the disruption of these aggregates could occur at high rates of shear. It can be seen that at shear rates approaching 1000 sec^{-1}, the viscosity becomes constant with increasing shear rate, implying that all flocculate bonds have been sheared.

The effect on the viscosity of the droplet aggregates is lower. At very high shear rates, the rheology of the deflocculated emulsion would approach that of a homogeneous dispersion with only hydrodynamic interaction of the emulsion droplets affecting the viscosity.

Time Dependence

An example of the time dependent nature of the oil-in-water emulsions is shown in Table A.1. In most cases, only a minor dependence of viscosity on the length of time of shear rate was found. The examples cited in Appendix A such as the change in the viscosity of the 12.0% oil-in-water Epping Emulsion from 2.82 Pa.s to 2.3 Pa.s, is the extreme rather than the average.

In the case of Epping oil-in-water emulsions, where time dependency was found, the rheological behaviour with time was thixotropic (the viscosity decreased with time). In the case of Cold Lake oil-in-water emulsions, where time dependency occurred, the behaviour was very slightly rheopectic (the viscosity increased slightly with time). No great significance is attributed to this behaviour because of the small magnitude of the changes. The magnitude of the viscosity measurement error would be of similar magnitude to the change in viscosity during the time dependent effects. In many cases (such as with water and dilute emulsions of oil-in-water) the time dependence was less than 1 sec to reach the stable maximum viscosity. This effect would be considered to be almost time independent.

Emulsion Correlation

The correlation by Richardson, as previously described was used in this study in an attempt to correlate the results. As previously mentioned, the log of the measured or apparent relative viscosity was plotted against the disperse phase concentration to see if the emulsion would behave according to Richardson's Correlation. This particular equation was chosen for simplicity of implementation and for its previous use by authors in the study of crude oil emulsion behaviour.

It can be seen from Figure A.19, A.20 and A.21 that the graph of Richardson's correlation of log relative viscosity (emulsion viscosity/external viscosity) vs. disperse phase concentration is not linear as the equation would predict. Although some results appear to be relatively linear, it can be seen that the results depart drastically from linearity at low shear rates and large disperse phase concentrations.

It can be seen that the previous results by Alvarado and Marsden [54] follow the linear trend for oil-in-water emulsions (see Figure A.19). It should be noted that the range of shear rates investigated by Alvarado and Marsden were of the order of 10 to 100 times greater than in this study. Alvarado and Marsden used an emulsion of Chevron Mineral Oil No. 3 and 1% NaCl brine stabilized with Triton N-57. Although the data for the mineral oil and Cold Lake Oil are similar, the data for the Epping Oil varies significantly. This may be due in part to the long storage

time of the Epping Crude Oil which may have altered the properties of the crude oil by slow oxidation.

It should be noted that none of the literature described correlations can successfully predict the behaviour of the emulsion over the full range of disperse phase concentrations. This is due to the fact that correlations for the relative viscosity dependency on disperse phase concentration do not take into account the shear rates at which viscosity is measured. Literature correlations have been quoted or implied for Newtonian fluids only.

Figure A.20 and A.21 show that at low disperse phase concentrations (below 10 to 20%) the dependency of viscosity on shear rate is very small which implies Newtonian behaviour. At this point the relation of log relative viscosity vs. disperse phase concentration is also linear which supports the contention that the correlation is valid only for Newtonian behaviour.

E. WATER-IN-OIL EMULSION RHEOLOGY

Both the Epping and Cold Lake Emulsions have similar rheological behaviour. Dried Epping Crude Oil and its water-in-oil emulsions are shown in Figures A.7, A.8, A.9, A.10 and A.11 respectively. Dried Cold Lake Crude Oil and its water-in-oil emulsions are shown in Figures A.13, A.14, A.15, A.16 and A.17 respectively. The emulsions at 10 to 20% water-in-oil concentration show a slight pseudoplastic

behaviour. At higher concentrations of 30 to 40% water-in-oil, the pseudoplastic behaviour becomes very noticeable with some emulsions showing a reduction in viscosity of 300 times over a shear rate of 1.0 to 1000.0 sec^{-1} at a constant temperature. Figure 5.4 (copied from Figure A.11) shows the large reduction in viscosity for lower temperatures of 20 to 30°C.

A possible explanation for this effect could involve the reversal or inversion of the emulsion. This process would have to be completely reversible with changing shear rate and time (as opposed to the usual case of emulsion reversibility with an increase or decrease in disperse phase concentration). Mao [55] has stated that the inversion traps energy making the reverse process difficult if not impossible (as in a violation of the second law of thermodynamics).

Another possible explanation for the large viscosity change could be associated with a similar phenomenon to that reported by Hoffman [56] . The discontinuous change in viscosity is caused by a flow instability in which surfaces of spheres packed into ordered arrays at low shear rates break up into less ordered arrays of spheres at higher shear rates. The original observation by Hoffman was supported by the technique of white light diffraction. This was not possible to confirm because of the opaque nature of our crude oil systems. To explain the observed decrease in viscosity (cited in this report), the emulsion droplet

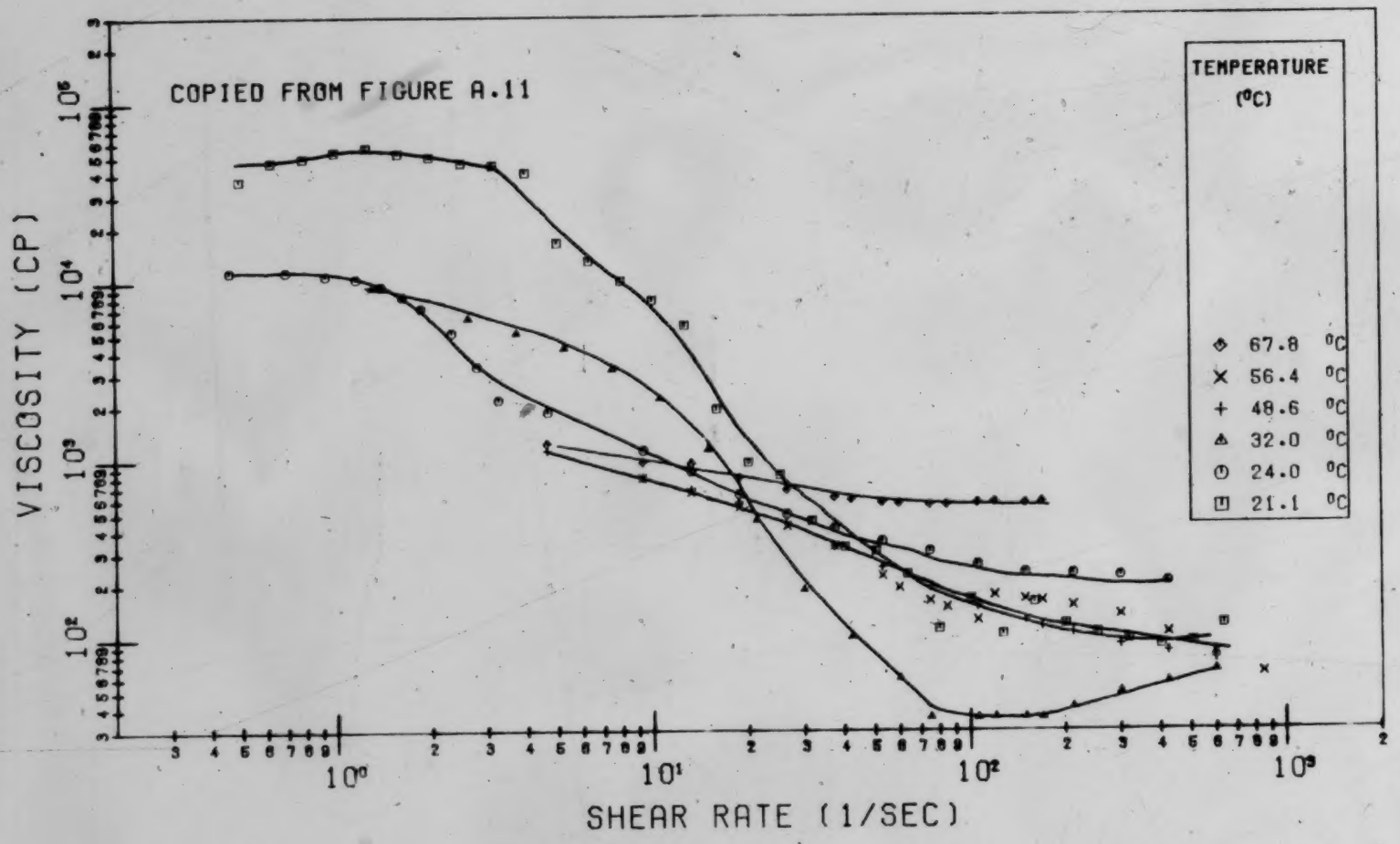


FIGURE 5.4 - RHEOLOGY OF 40.6% W/O EMULSION EPPING CRUDE OIL

packing would go from a less ordered to a more ordered array (to produce a drop in the observed viscosity). This explanation still would not account for the decrease in apparent viscosity below that of the original oil viscosity.

The observed decrease would still imply some type of emulsion inversion (where the water would become the continuous phase). The photograph of the emulsion immediately after the observed drop in viscosity (see Plate C.15) supports the contention that the emulsion has changed from a water-in-oil emulsion to a water-in-oil-in-water emulsion. This "inversion" is different from a simple inversion of water-in-oil to oil-in-water or vice versa. The process could possibly be better defined as the production of a dual emulsion from a single emulsion rather than an inversion.

Epping Water-in-Oil Emulsions

The water-in-oil emulsions of Epping Crude Oil display a decrease in apparent viscosity with increasing shear rate. The magnitude of the apparent viscosity decrease also appears to become greater as the percentage of disperse phase concentration is increased. The rheology of the 9.5% water-in-oil Epping Crude Oil emulsion is very similar to the dried Epping Crude Oil emulsion except that the decrease in apparent viscosity with shear rate is slightly greater for the 9.5% emulsion. The degree of viscosity drop with shear rate (pseudoplasticity) increases until the concentrations of 30 to 40% are reached. The viscosity then

displays a large drop which would be associated with the inversion process at high shear rates.

A plot of an ASTM type temperature-viscosity relation is shown in Figure A.22 and A.24 for Epping Oil (at shear rates of 1.0 and 100.0 sec^{-1} respectively). In general, at lower shear rates the viscosity declines linearly with temperature as would be predicted. At higher concentrations of water-in-oil and higher shear rates the temperature-viscosity relation becomes a constant (the viscosity becomes almost independent of temperature). This effect is the result of the inversion type process which appears to reduce the viscosity to a similar value regardless of the original apparent viscosity before the inversion process began.

Cold Lake Water In Oil Emulsions

Cold Lake Dried Crude exhibits a Newtonian or slightly dilatant behaviour (viscosity constant or slightly increasing with shear rate), which is in contrast to the pseudoplastic behaviour (viscosity decrease with shear rate) of its emulsions. The behaviour of the Cold Lake Emulsions is very similar to the previous emulsions of Epping Crude Oil, although the two dried crude oils have slightly different rheologies.

The Cold Lake Emulsions also display an increasing pseudoplastic behaviour of apparent viscosity increase with shear rate as the concentration of disperse phase is increased. Again the rheology of the 10.4% water-in-oil

emulsion is very similar to the dried oil at corresponding temperatures except that the viscosity decrease with shear rate is slightly greater for the 10.4% emulsion. As with the Epping Crude Oil Emulsions, the large viscosity drop at high shear rates for the 30.1 and 38.3% water-in-oil emulsions are probably associated with a similar inversion process.

A plot of an ASTM type temperature-viscosity relation is shown in Figure A.23 and A.25 for Cold Lake Oil (at shear rates of 1.0 and 100.0 sec^{-1} respectively). The general trend is similar to the Epping Crude. At lower shear rates the apparent viscosity declines linearly with temperature but at higher concentrations of water-in-oil and higher shear rates the apparent viscosity becomes a constant.

Time Dependence

In general, the emulsions of water-in-oil are time independent with the exception of the time dependent effects near the inversion point. An example of the time dependent nature of the water-in-oil emulsions at the inversion point are shown in Table A.2.

The time dependent behaviour (as shown in Table A.2) was repeated several times to insure reproducibility. The emulsion showed the greatest time dependency at the shear rate corresponding to the inversion point. The time dependent nature of the water-in-oil emulsions would probably be caused by the length of time necessary to cause the minor inversion to occur.

Emulsion Viscosity Correlation

For the water-in-oil emulsions, an attempt was made to correlate the emulsion viscosity with the disperse phase concentration according to the equation by Richardson [57]. The plots of disperse phase concentration vs. relative viscosity are shown in Figures A.26, A.27, A.28 and A.29 for 1.0 sec^{-1} Epping and Cold Lake, and 100.0 sec^{-1} Epping and Cold Lake respectively. It is obvious that this equation cannot predict the apparent viscosity for phase concentrations of 30 to 40%. The reduction in viscosity associated with the inversion is a shear rate dependent effect and the correlations do not apply when the inversion occurs. The equation could predict the apparent viscosity only where the emulsion is mainly affected by hydrodynamic interaction of the emulsion droplets.

VI. CONCLUSIONS

Based upon the literature review, experimental observations and the analyses of the results of this investigation, the following conclusions have been formulated:

1. The rheology of both Epping and Cold Lake Crude oil-in-water emulsions with less than 15% disperse phase concentration behave in a Newtonian manner over the range of shear rates of 50 to 1000 sec^{-1} and room temperature. Oil-in-water emulsions with 15% oil-in-water and greater can behave as non-Newtonian fluids at the low end of shear rates 50 to 1000 sec^{-1}.
2. Both Cold Lake and Epping water-in-oil emulsions with as little as 20% disperse phase concentration behave as non-Newtonian fluids but are generally non-Newtonian only at higher shear rates from 100 to 1000 sec^{-1}.
3. The Epping Crude oil-in-water emulsions appear to follow the Richardson's correlation at disperse phase concentrations of less than 10% by volume. The Cold Lake Crude oil-in-water emulsions appear to follow the correlation at disperse phase concentrations of less than 20% by volume. The Cold Lake water-in-oil emulsions also tend to follow the correlation but only at shear rates of about 1.0 sec^{-1}.
4. Although the Epping and Cold Lake Crude Oils have a similar viscosity, density and rheology, the rheological behaviour of their emulsions are significantly different.

5. The emulsions are shown to be relatively time independent except for water-in-oil emulsions near the inversion point.

VII. RECOMMENDATIONS

1. To continue to study other emulsions prepared under different methods to validate the correlation for a general system.
2. To study emulsion systems produced from oilfields to compare their rheology with synthetically prepared emulsions.

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APPENDIX A

TABLE A.1 - Rheological Behavior of Oil-in-Water Emulsions

Epping Emulsions

Time (sec)	Viscosity of 12.2% O/W (@506 sec^{-1}) (Pa.s)	Viscosity of 35.2% O/W (@506 sec^{-1}) (Pa.s)
0.0	2.82	10.8
30.0	2.57	10.6
60.0	2.46	10.5
120.0	2.33	10.4
180.0	2.30	10.3
240.0	2.30	10.3

NOTE: thixotropic behaviour

Cold Lake Emulsions

Time (sec)	Viscosity of 11.2% O/W (@1007 sec^{-1}) (Pa.s)	Viscosity of 39.0% O/W (@635 sec^{-1}) (Pa.s)
0.0	1.20	3.87
15.0	1.22	3.89
30.0	1.23	3.90
45.0	1.24	3.91
60.0	1.24	3.92

NOTE: slight rheopectic behaviour

TABLE A.2 - Rheological Behavior of Water-in-Oil Emulsions

38.3% Water-in-Oil Cold Lake Emulsion

Time (sec)	Viscosity (Pa.s) (@6.36 sec^{-1})	Viscosity (Pa.s) (@8.01 sec^{-1})
0.0	35350	19518
30.0	22850	10302
60.0	19221	9666
90.0	16398	9117
120.0	14920	8628
180.0	13441	8219
240.0	13441	8042

40.6% Water-in-Oil Epping Emulsion

Time (sec)	Viscosity (Pa.s) (@5.06 sec^{-1})	Viscosity (Pa.s) (@6.36 sec^{-1})
0.0	37205	26419
30.0	29618	19136
60.0	24040	15835
120.0	17598	13556
180.0	16602	13098
240.0	16602	13098

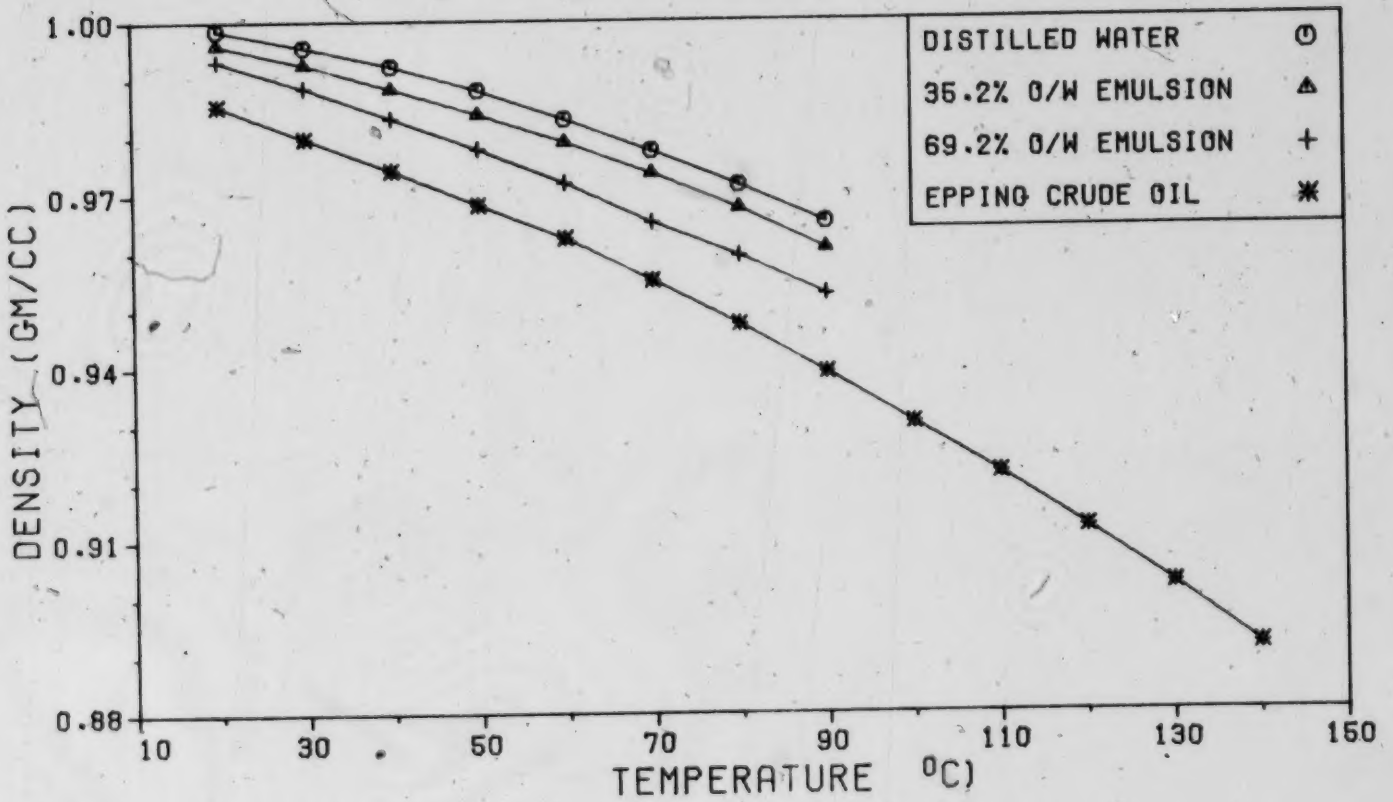

FIGURE A.1 - O/W EMULSION DENSITIES
EPPING CRUDE OIL

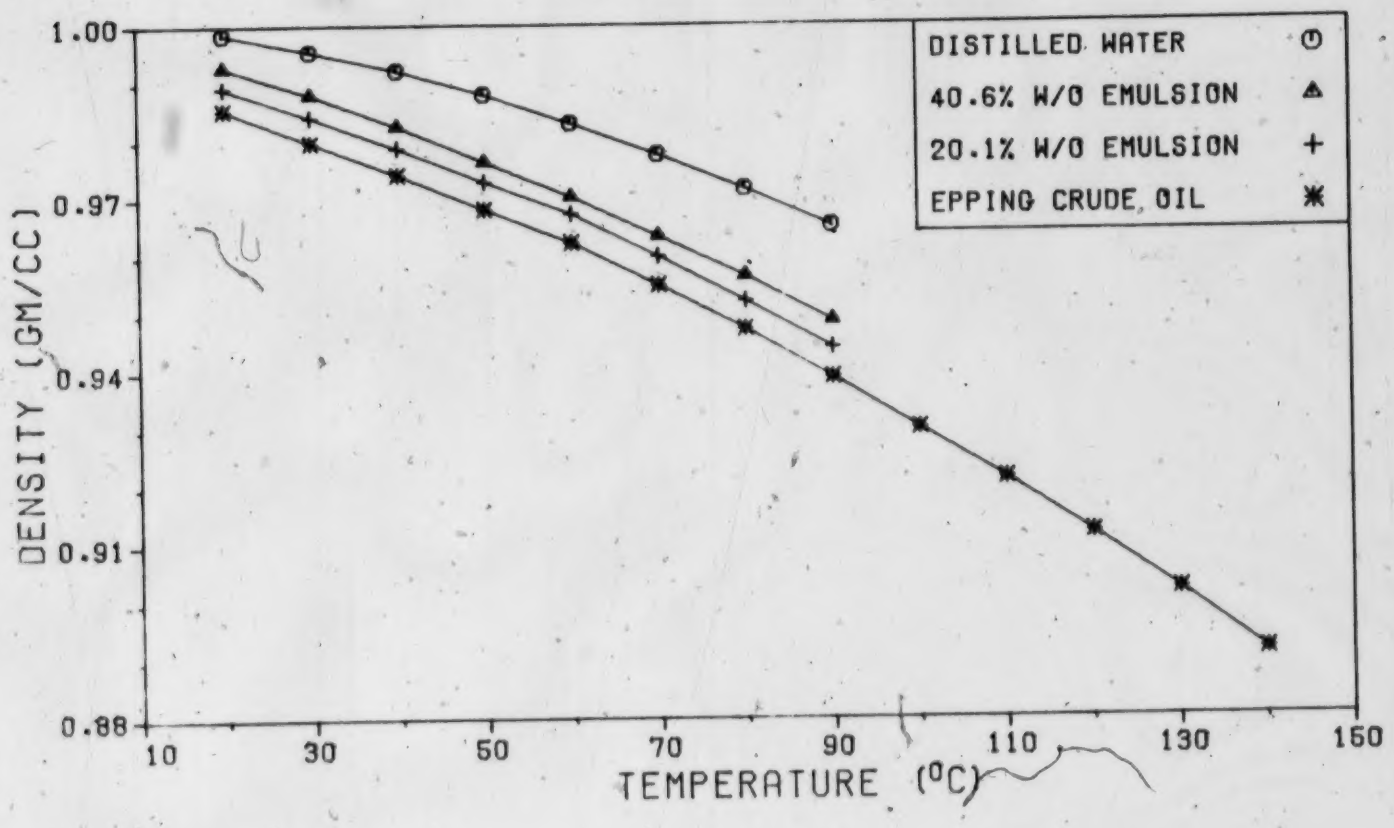

FIGURE A.2 - W/O EMULSION DENSITIES
EPPING CRUDE OIL

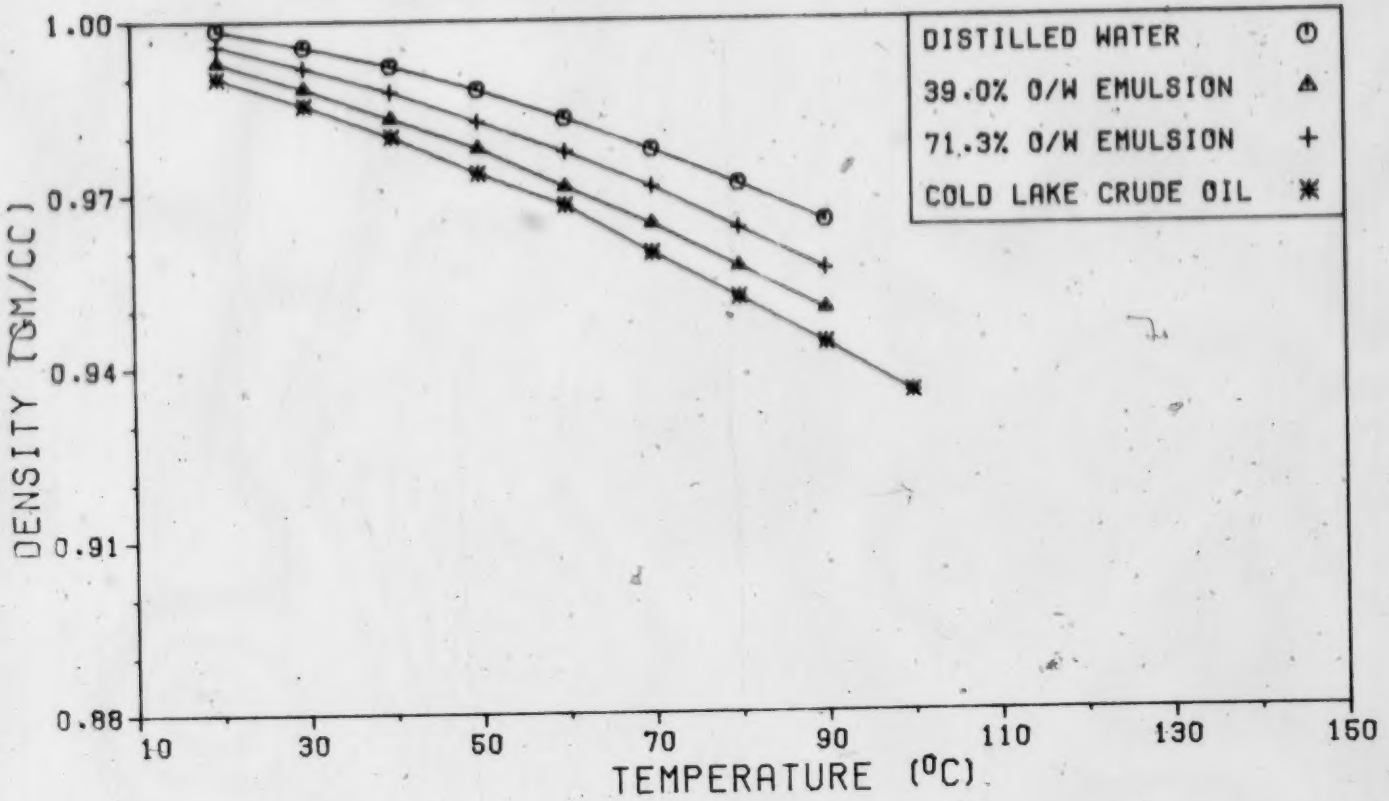

FIGURE A.3 - O/W EMULSION DENSITIES
COLD LAKE CRUDE OIL

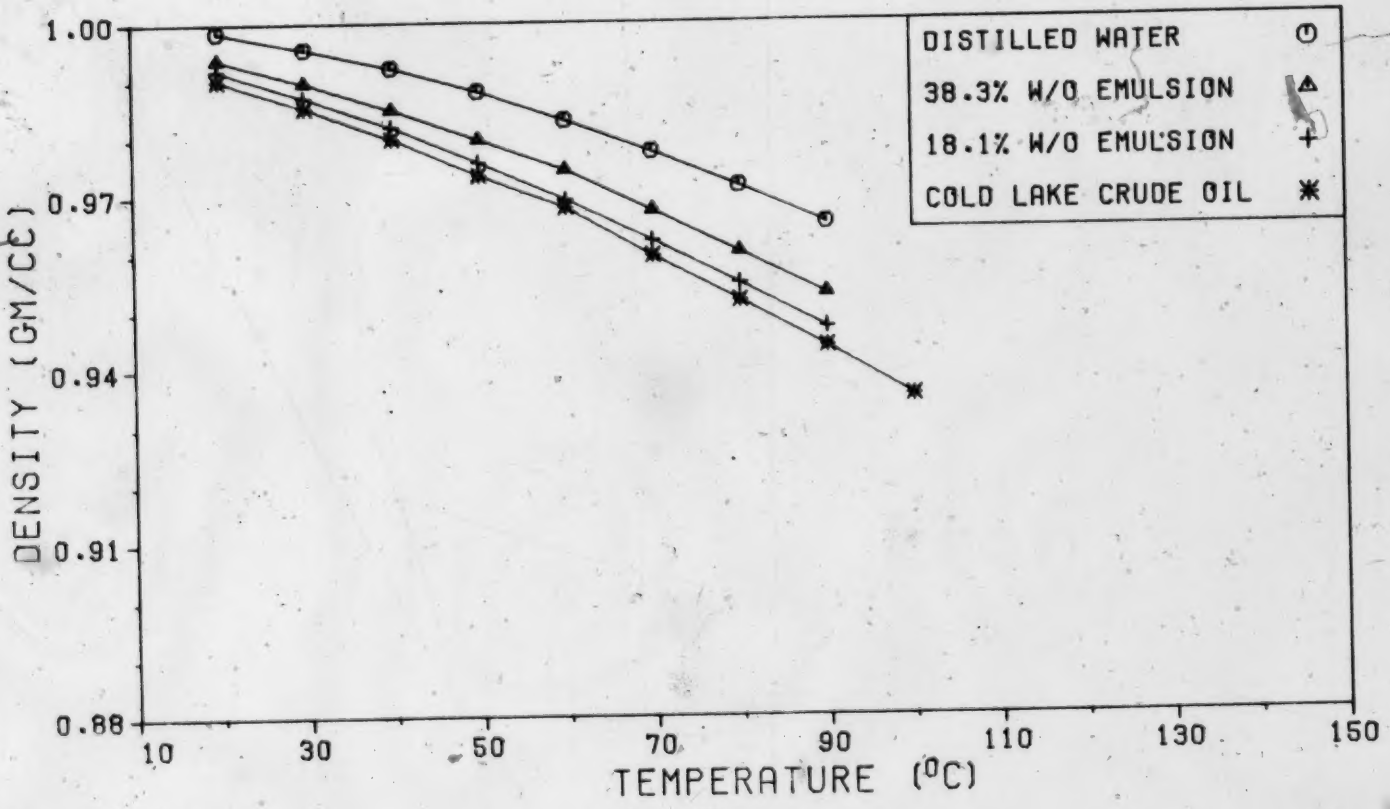

FIGURE A.4 - W/O EMULSION DENSITIES
COLD LAKE CRUDE OIL

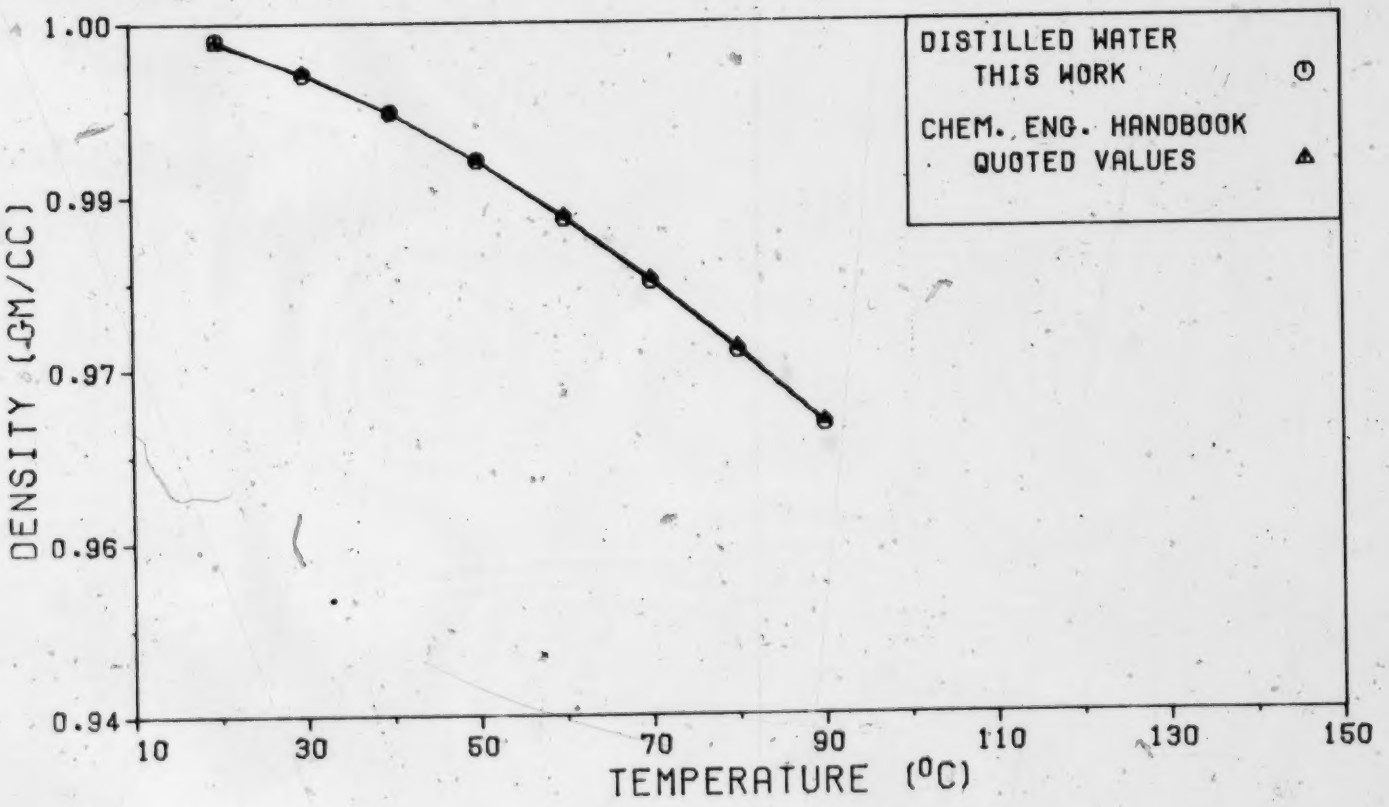

FIGURE A.5 - DENSITY OF DISTILLED WATER

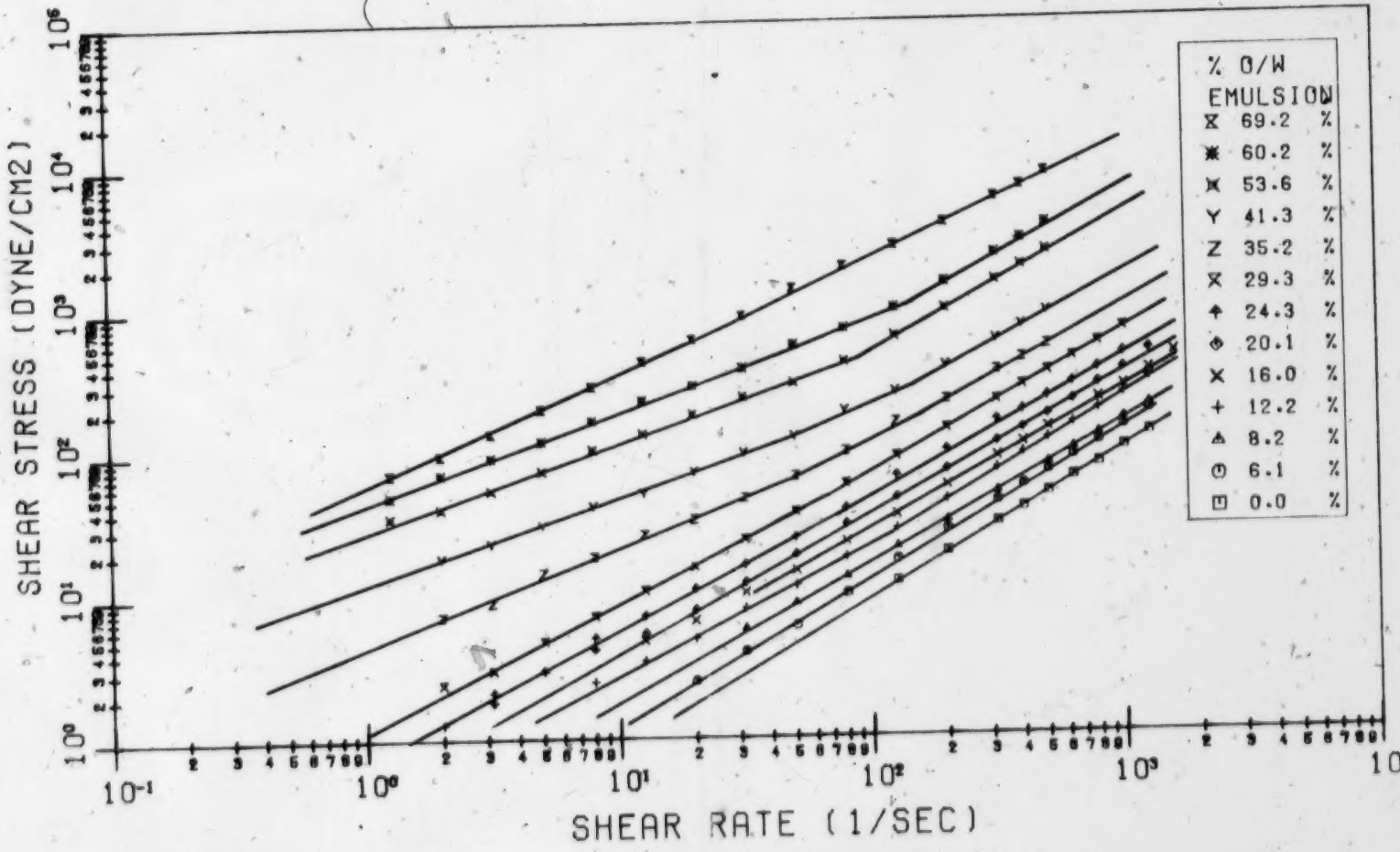

FIGURE A.6 - RHEOLOGY OF O/W EMULSIONS
EPPING CRUDE OIL

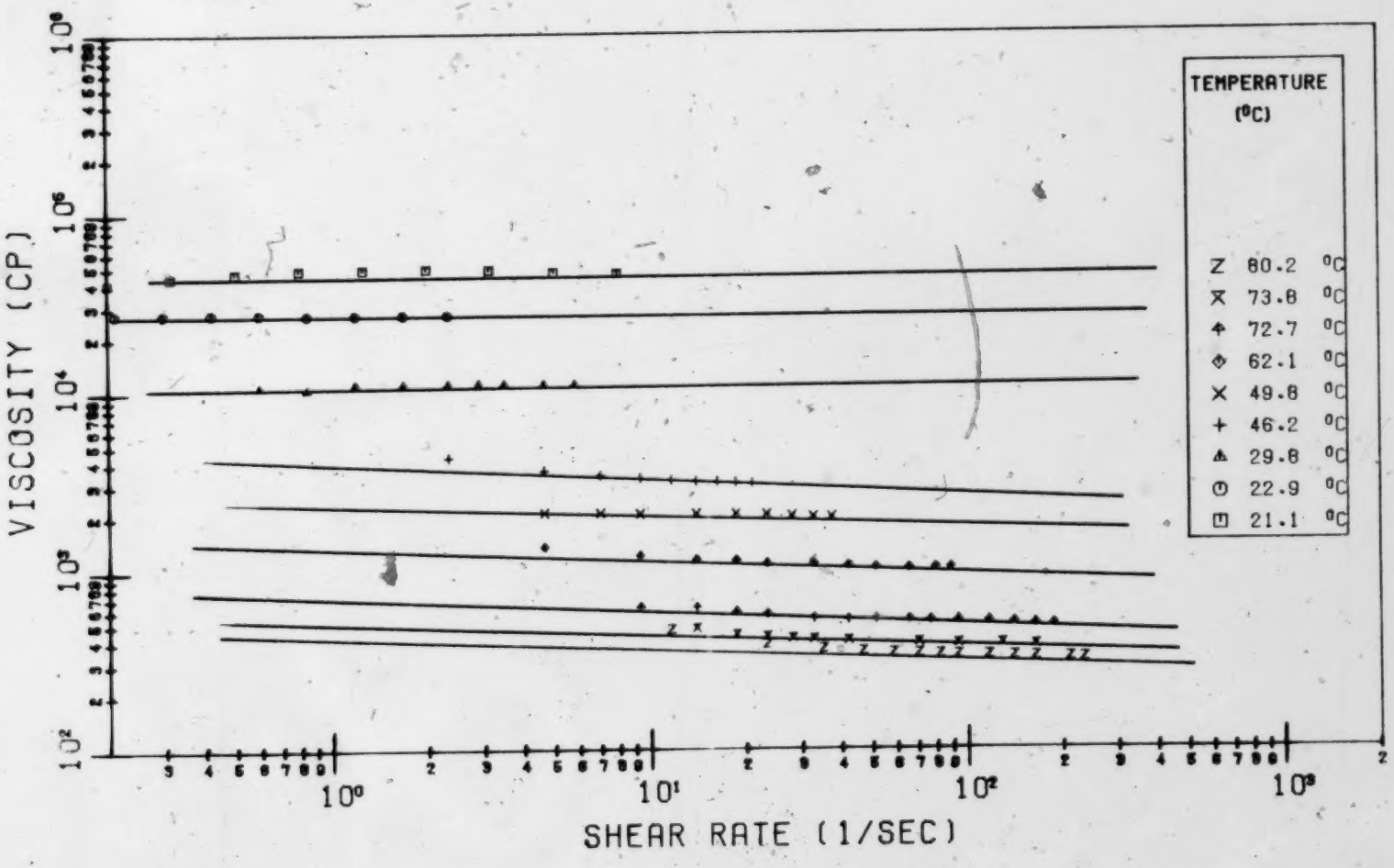

FIGURE A.7 - RHEOLOGY OF DRIED CRUDE OIL EPPING CRUDE OIL

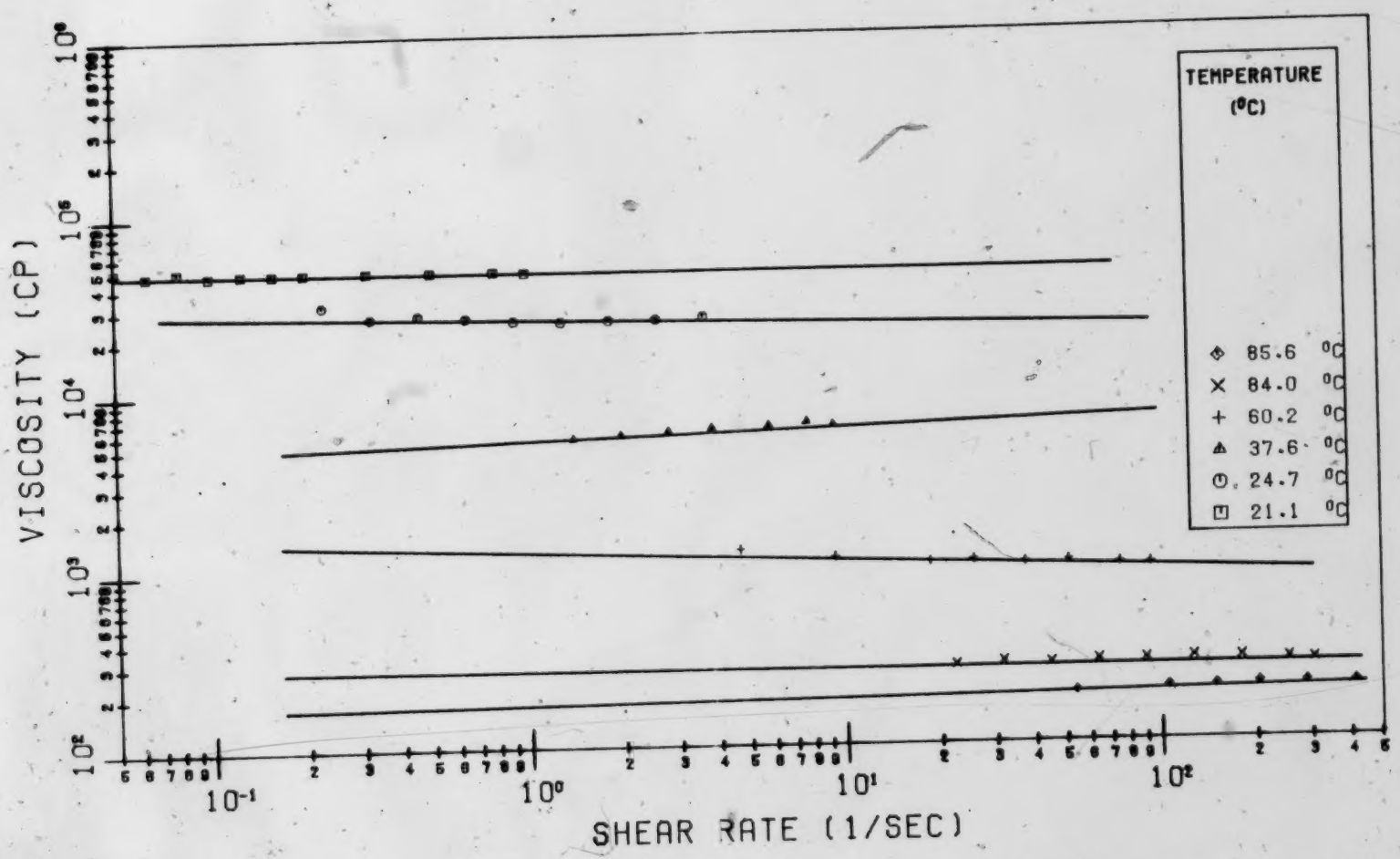

FIGURE A.8 - RHEOLOGY OF 9.5% W/O EMULSION EPPING CRUDE OIL

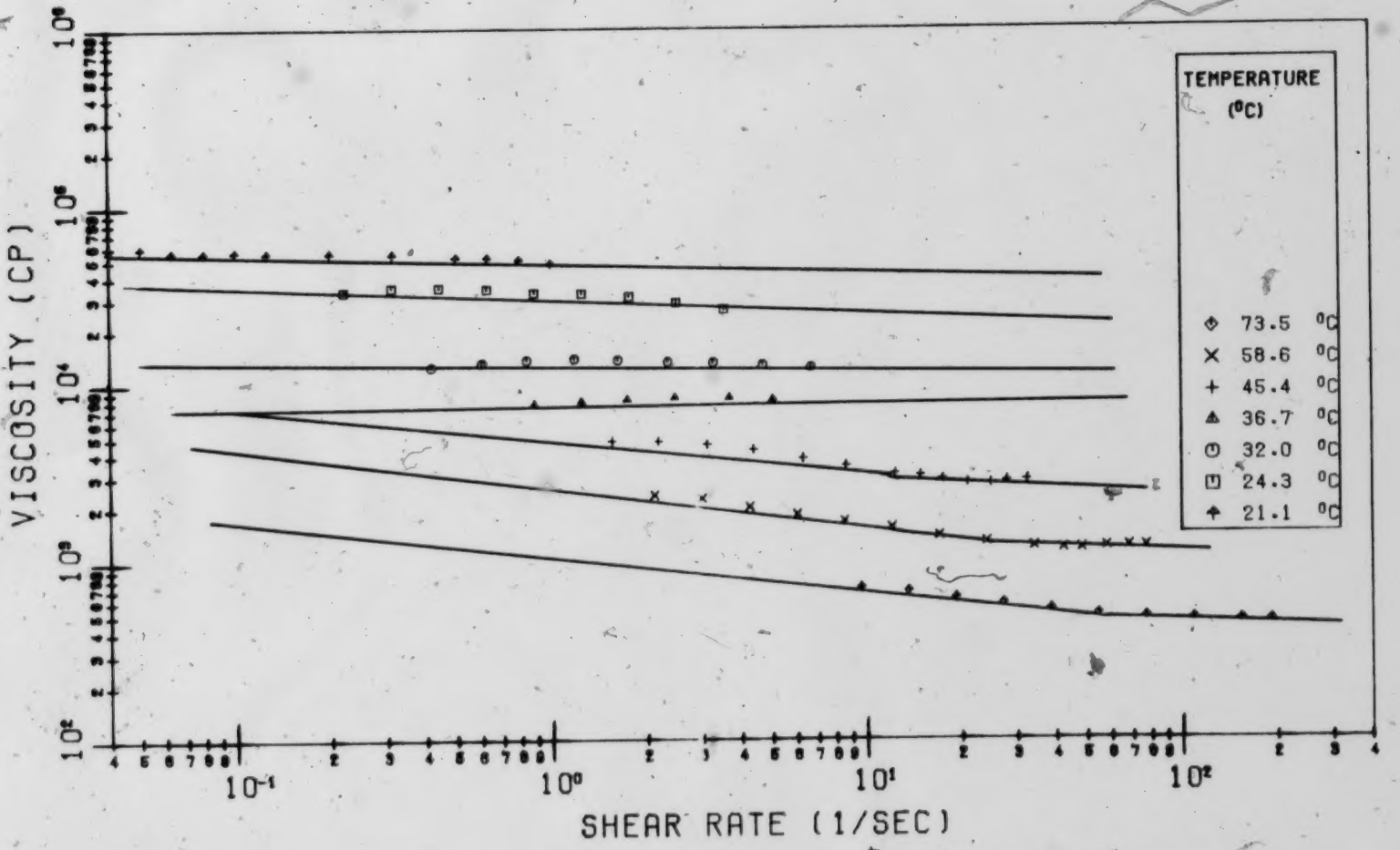

FIGURE A.9 - RHEOLOGY OF 20.1% W/O EMULSION EPPING CRUDE OIL

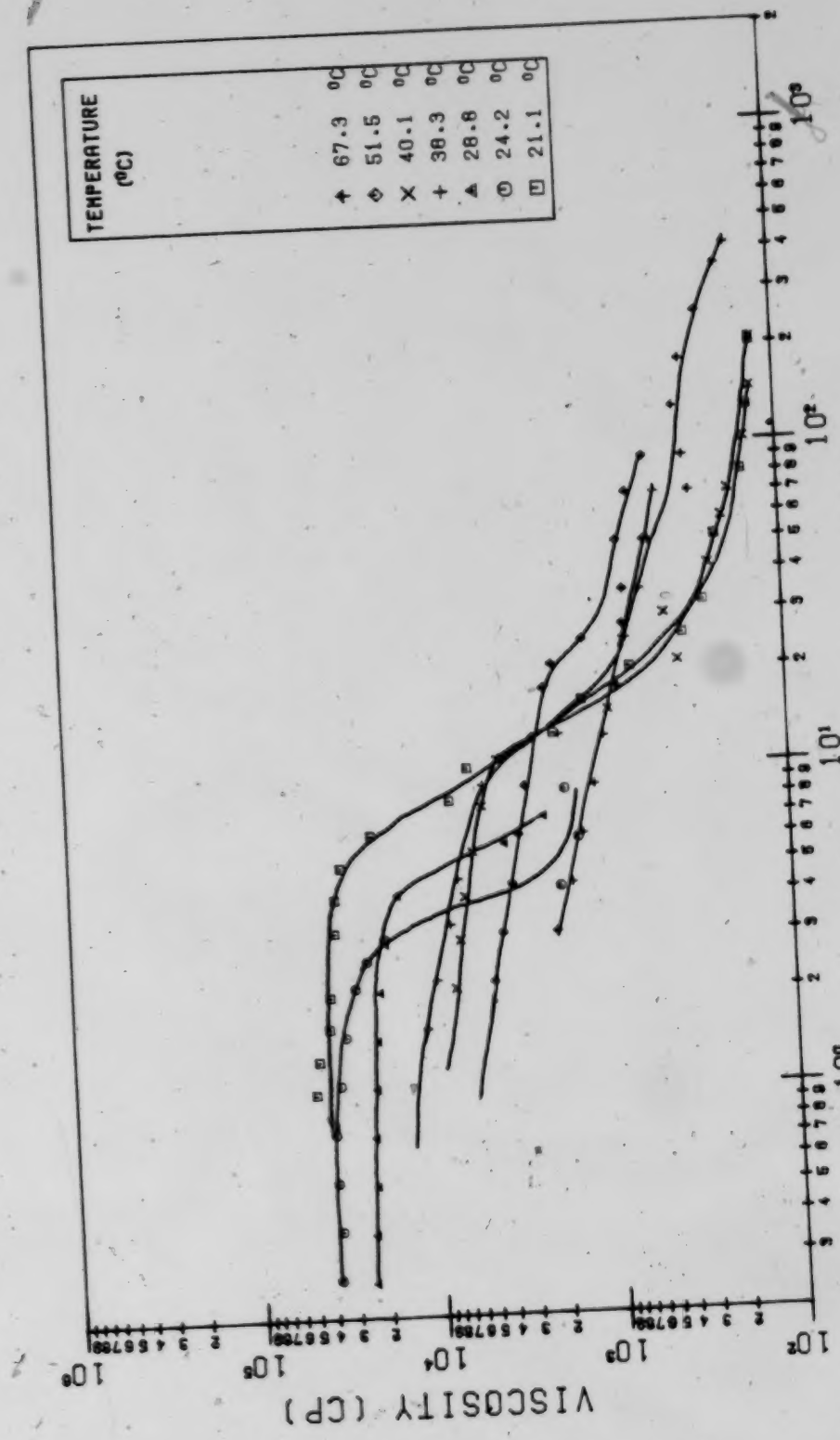

FIGURE A.10 - RHEOLOGY OF 30.3% W/O EMULSION
EPPING CRUDE OIL

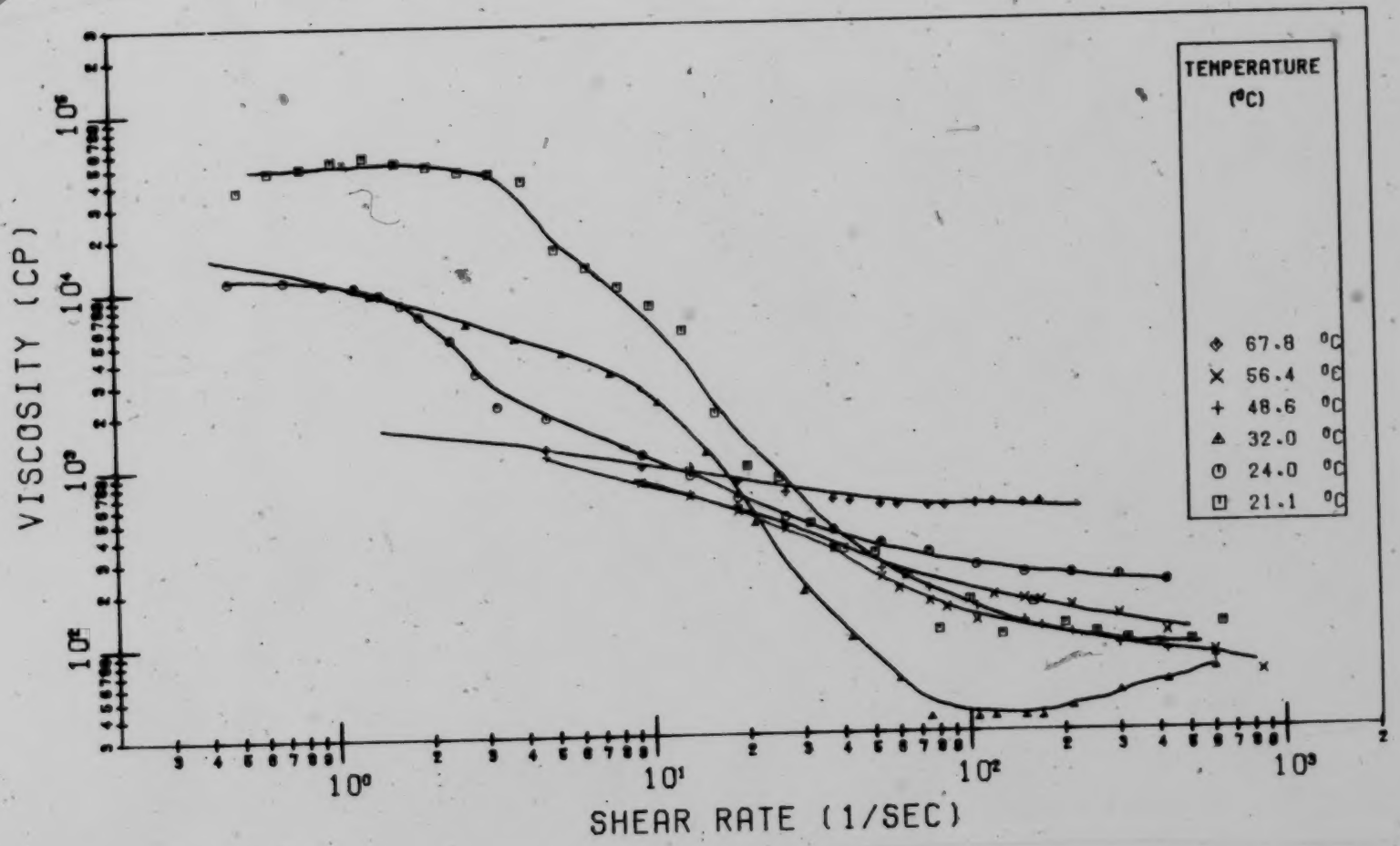

FIGURE A.11 - RHEOLOGY OF 40.6% W/O EMULSION EPPING CRUDE OIL

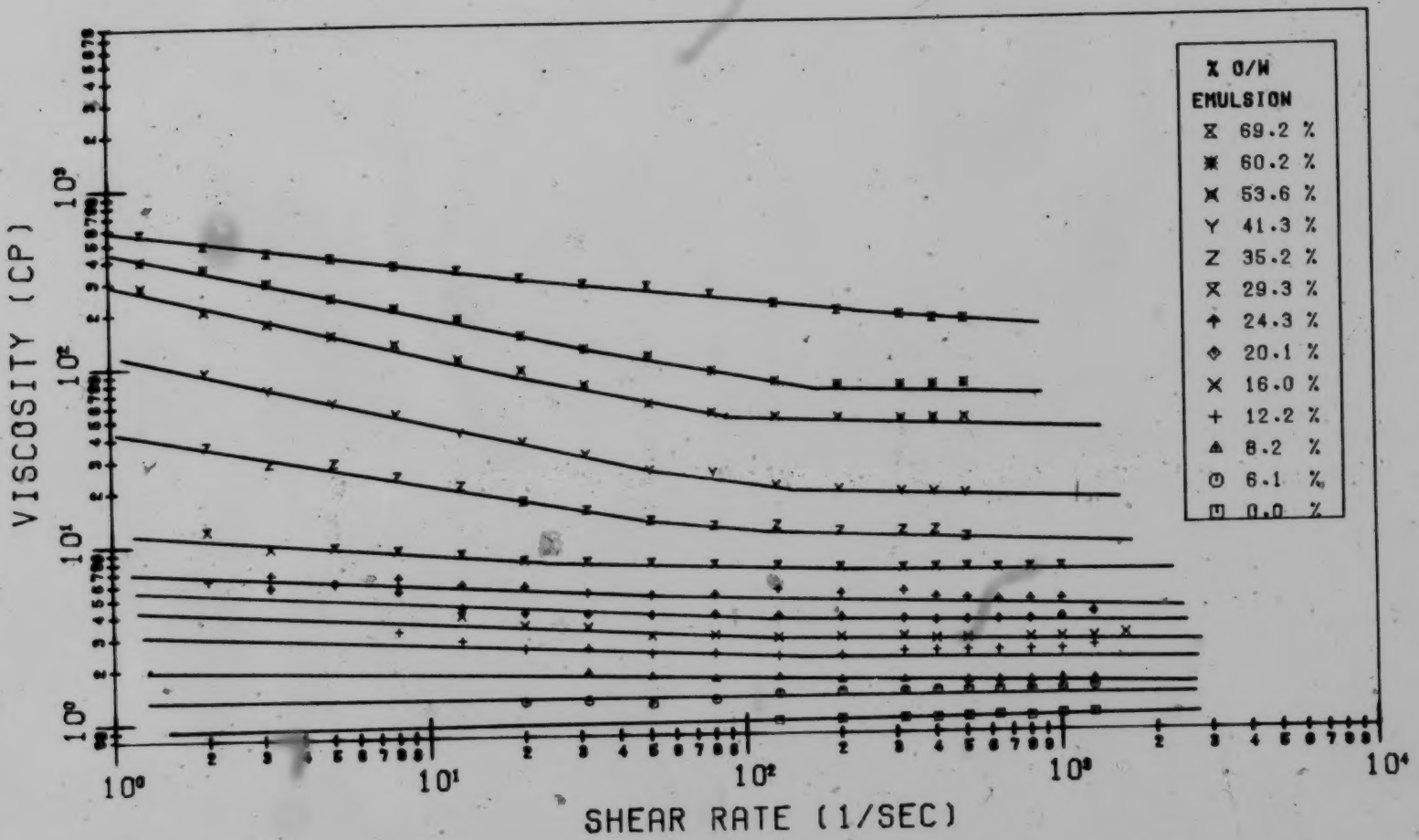

FIGURE A.12 - RHEOLOGY OF EPPING CRUDE O/W EMULSIONS AT ROOM TEMPERATURE

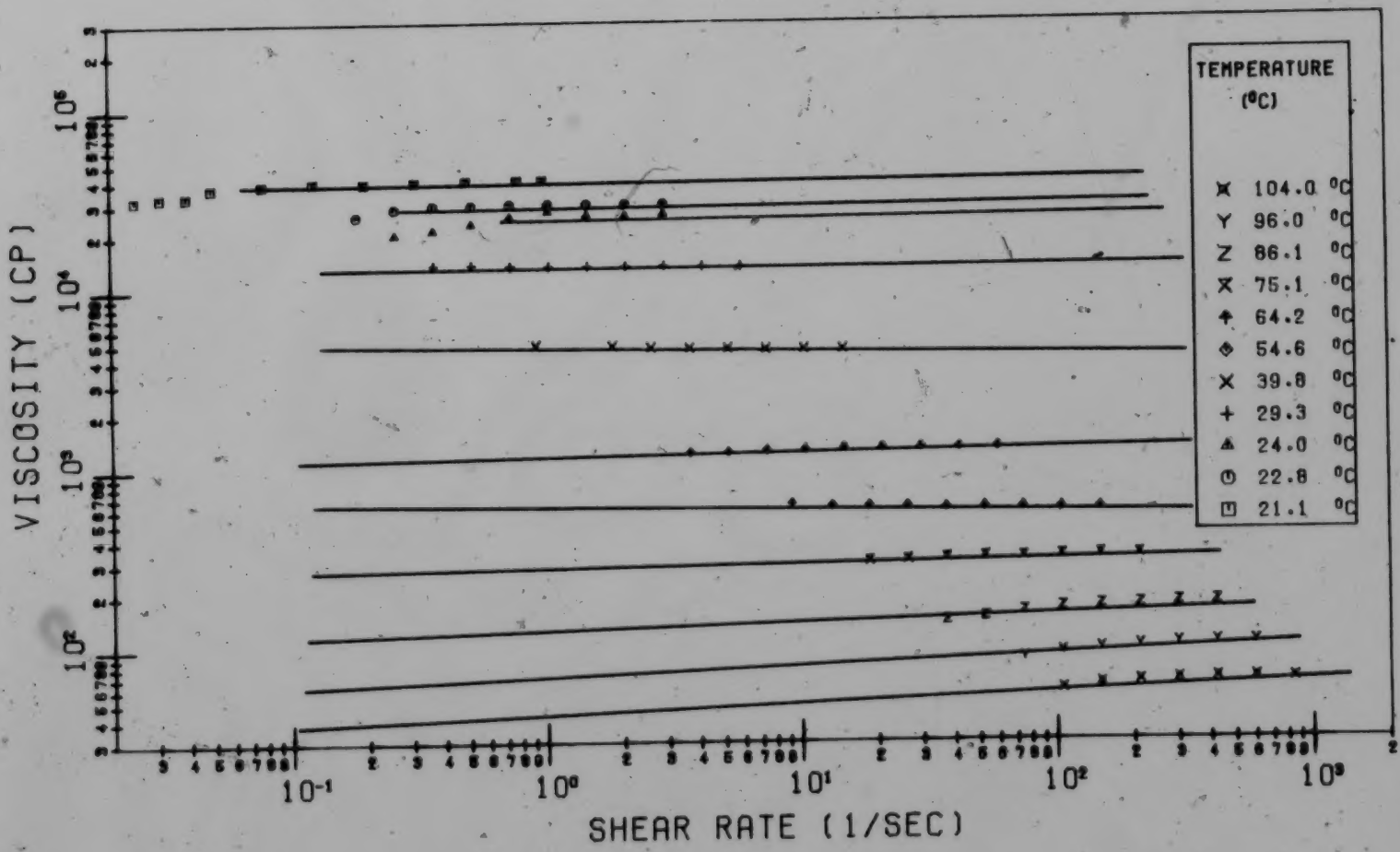

FIGURE A.13 – RHEOLOGY OF DRIED CRUDE OIL
COLD LAKE CRUDE OIL

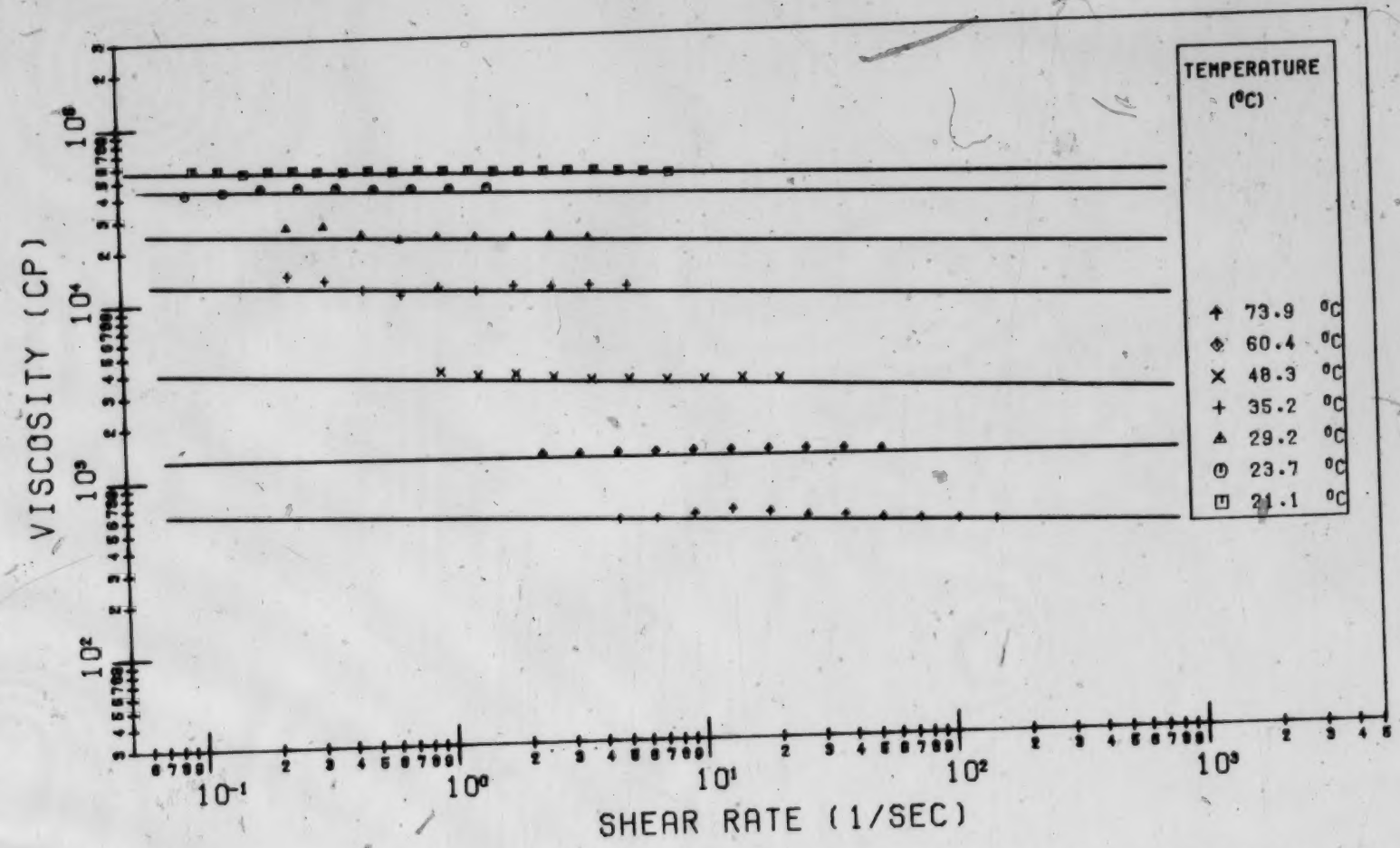

FIGURE A.14 -- RHEOLOGY OF 10.4% W/O EMULSION COLD LAKE CRUDE OIL

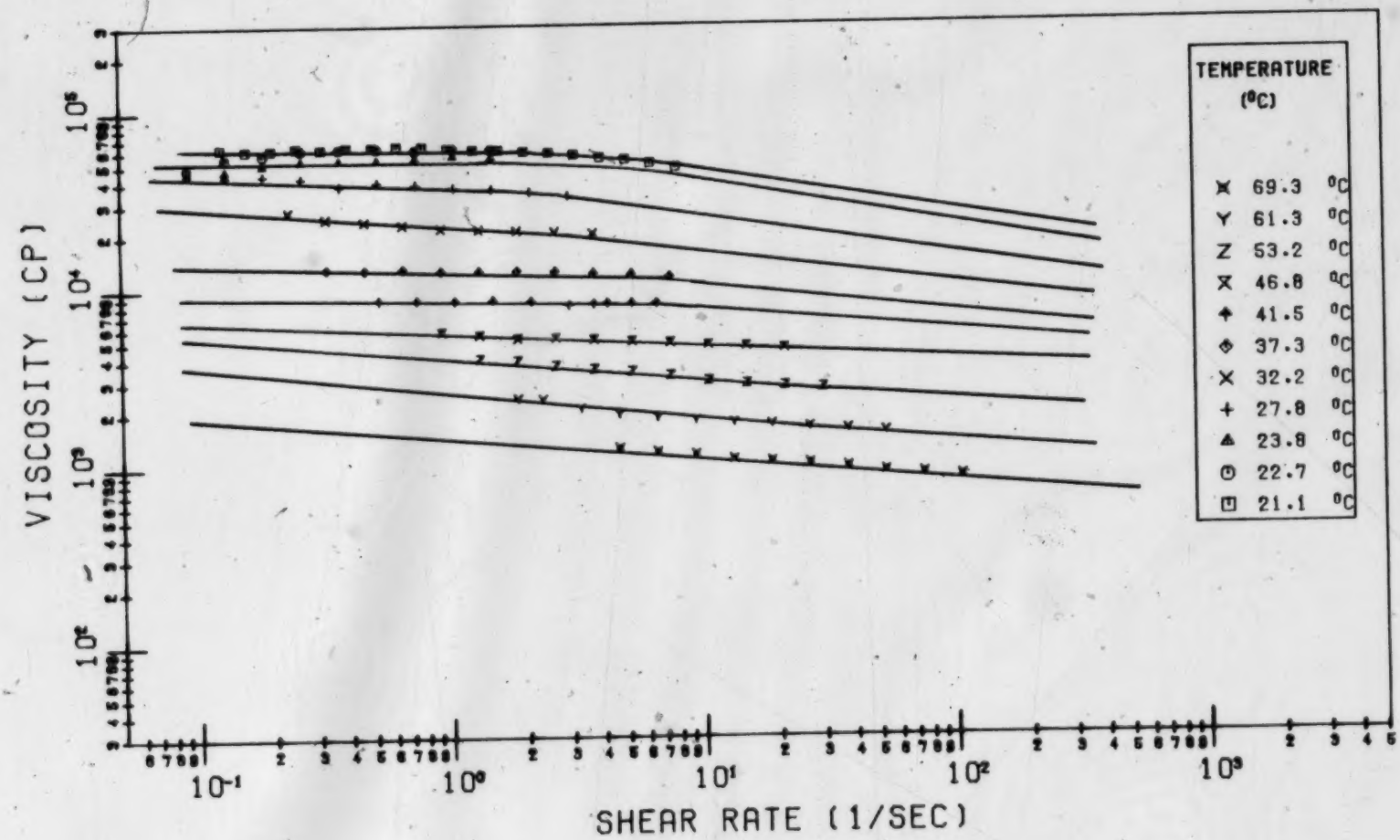

FIGURE A.15 - RHEOLOGY OF 18.1% W/O EMULSION
COLD LAKE CRUDE OIL

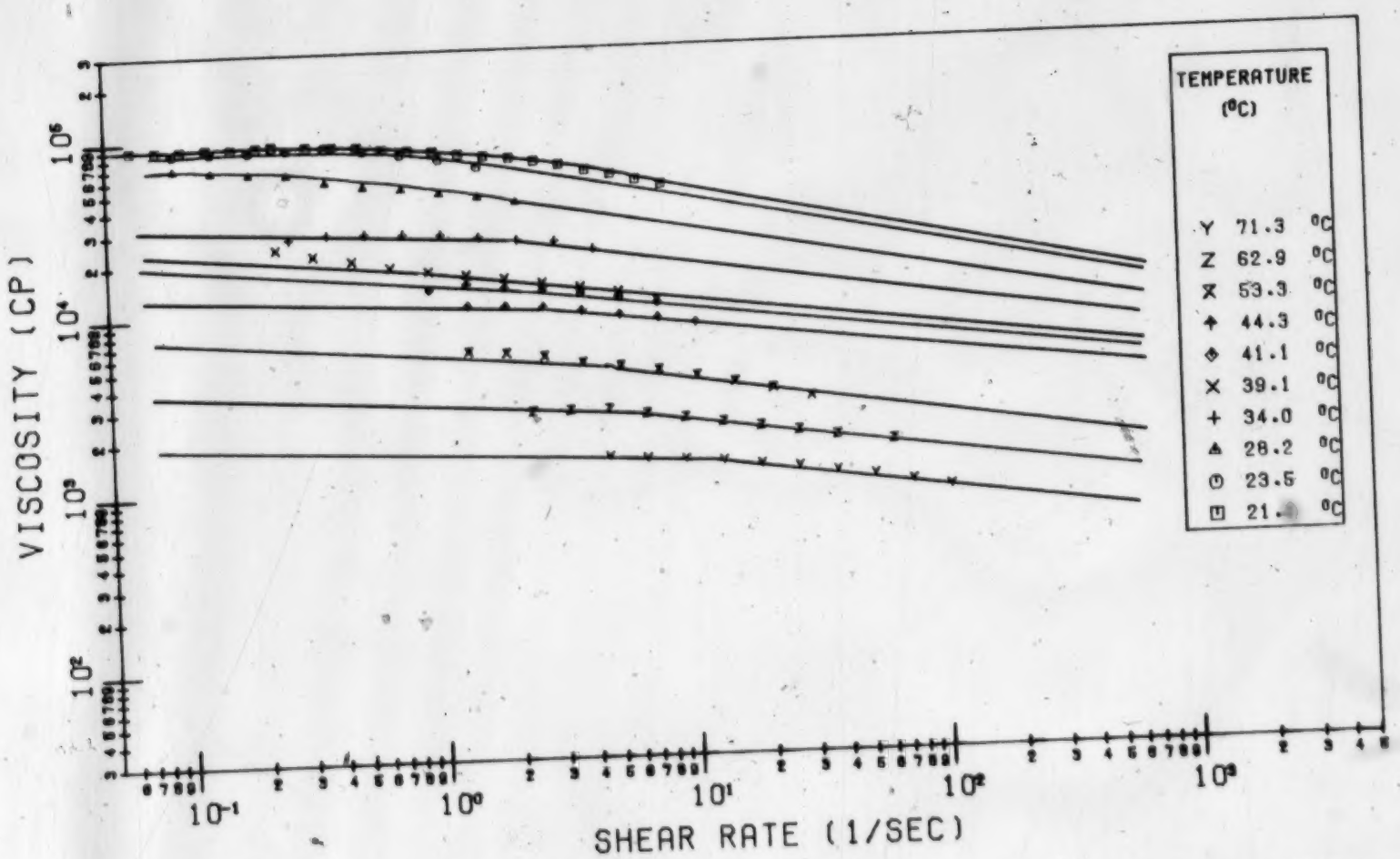

FIGURE A.16 - RHEOLOGY OF 30.1% W/O EMULSION
COLD LAKE CRUDE OIL

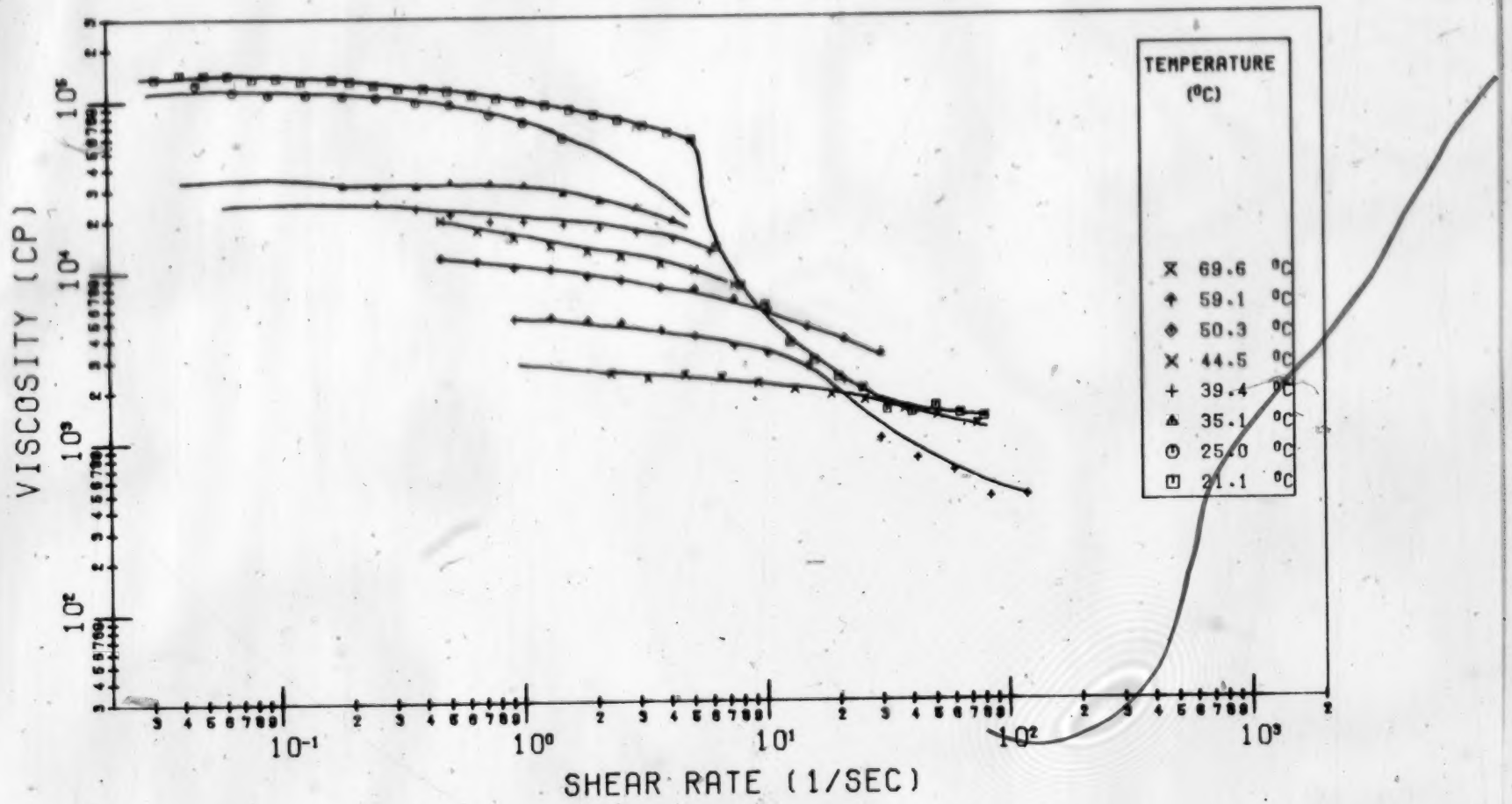

FIGURE A.17 - RHEOLOGY OF 38.3% W/O EMULSION COLD LAKE CRUDE OIL

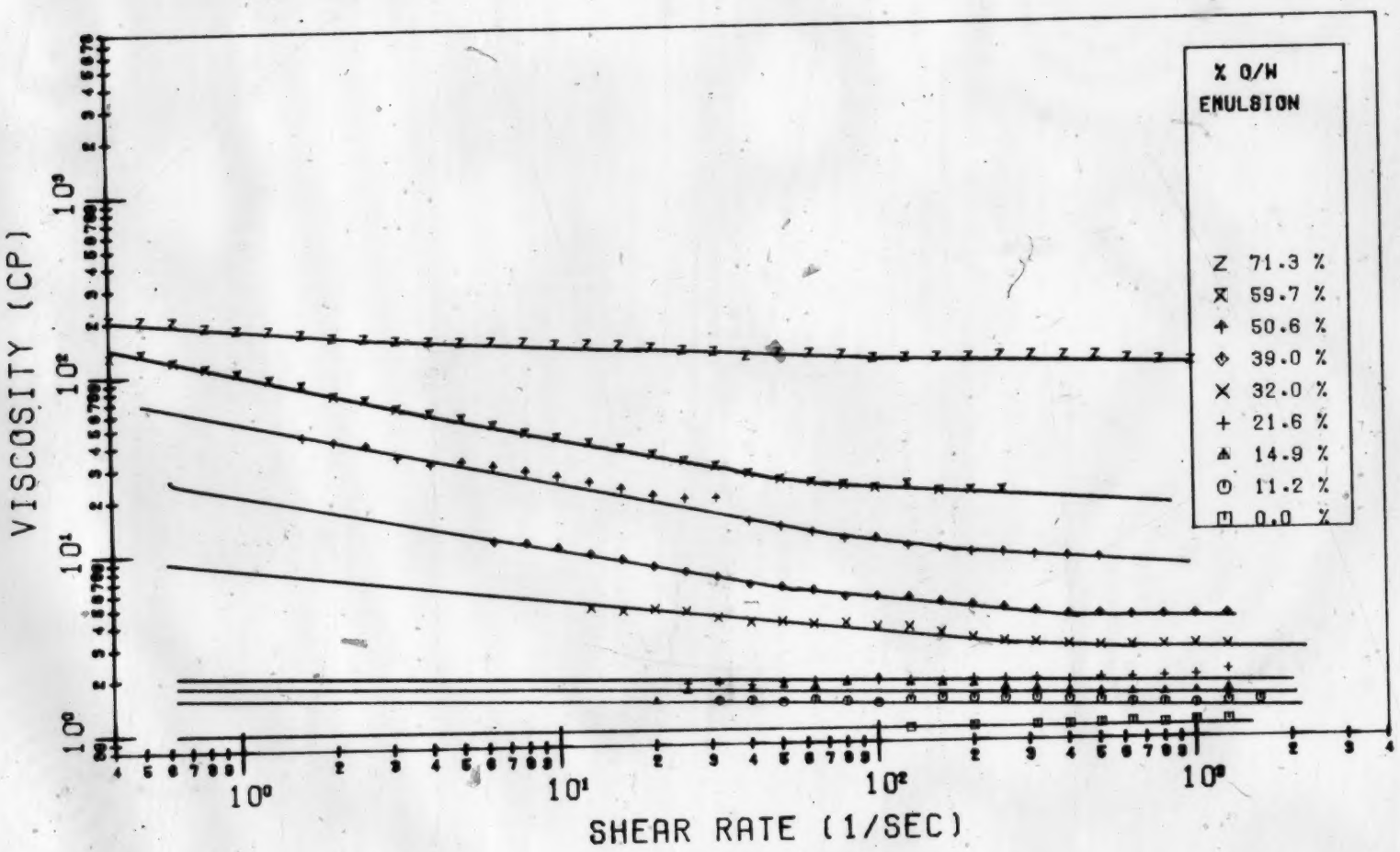

FIGURE A.18 - RHEOLOGY OF COLD LAKE O/W EMULSIONS AT ROOM TEMPERATURE

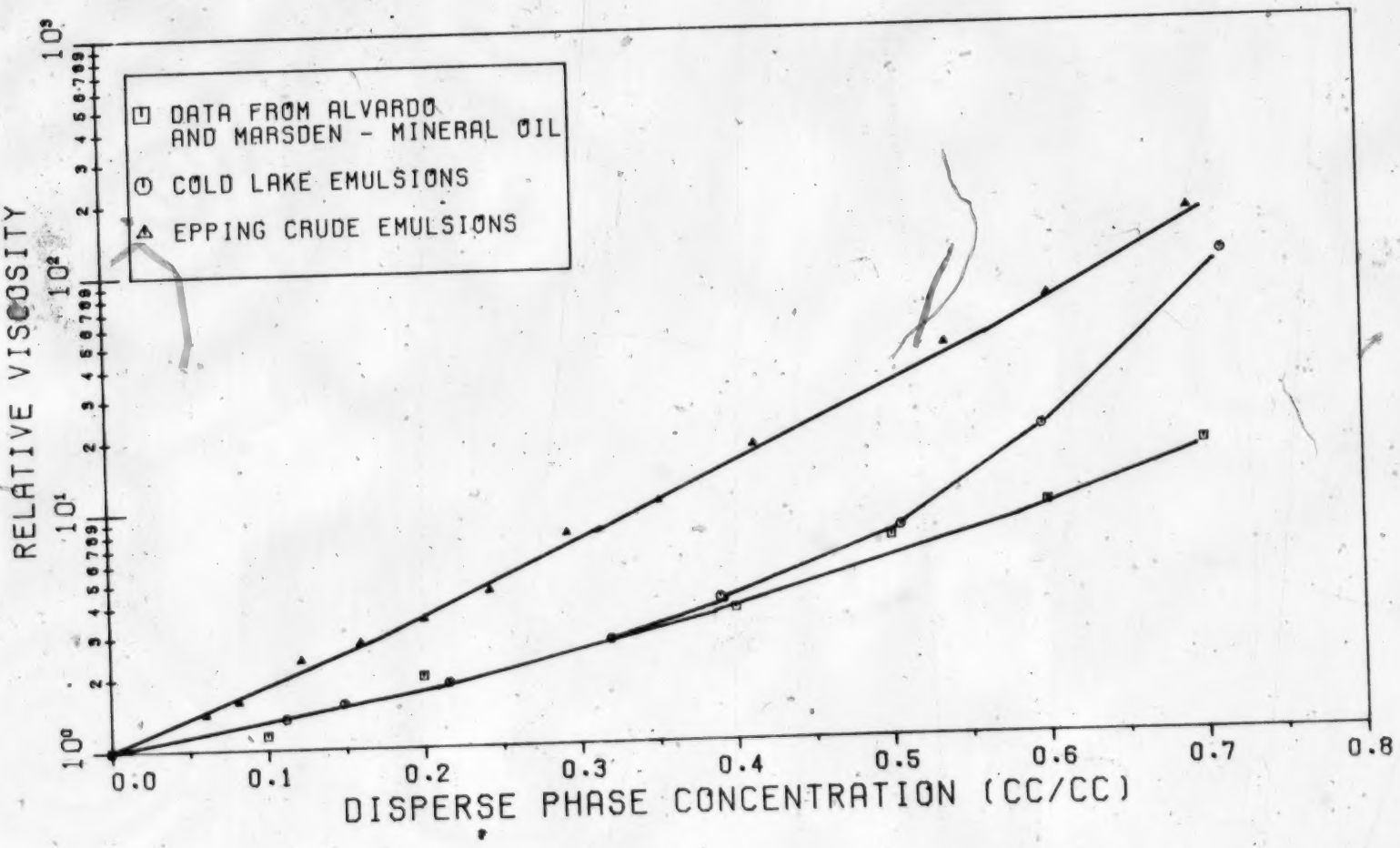

FIGURE A.19 - O/W EMULSION CORRELATION AT A SHEAR RATE OF 1000 1/SEC

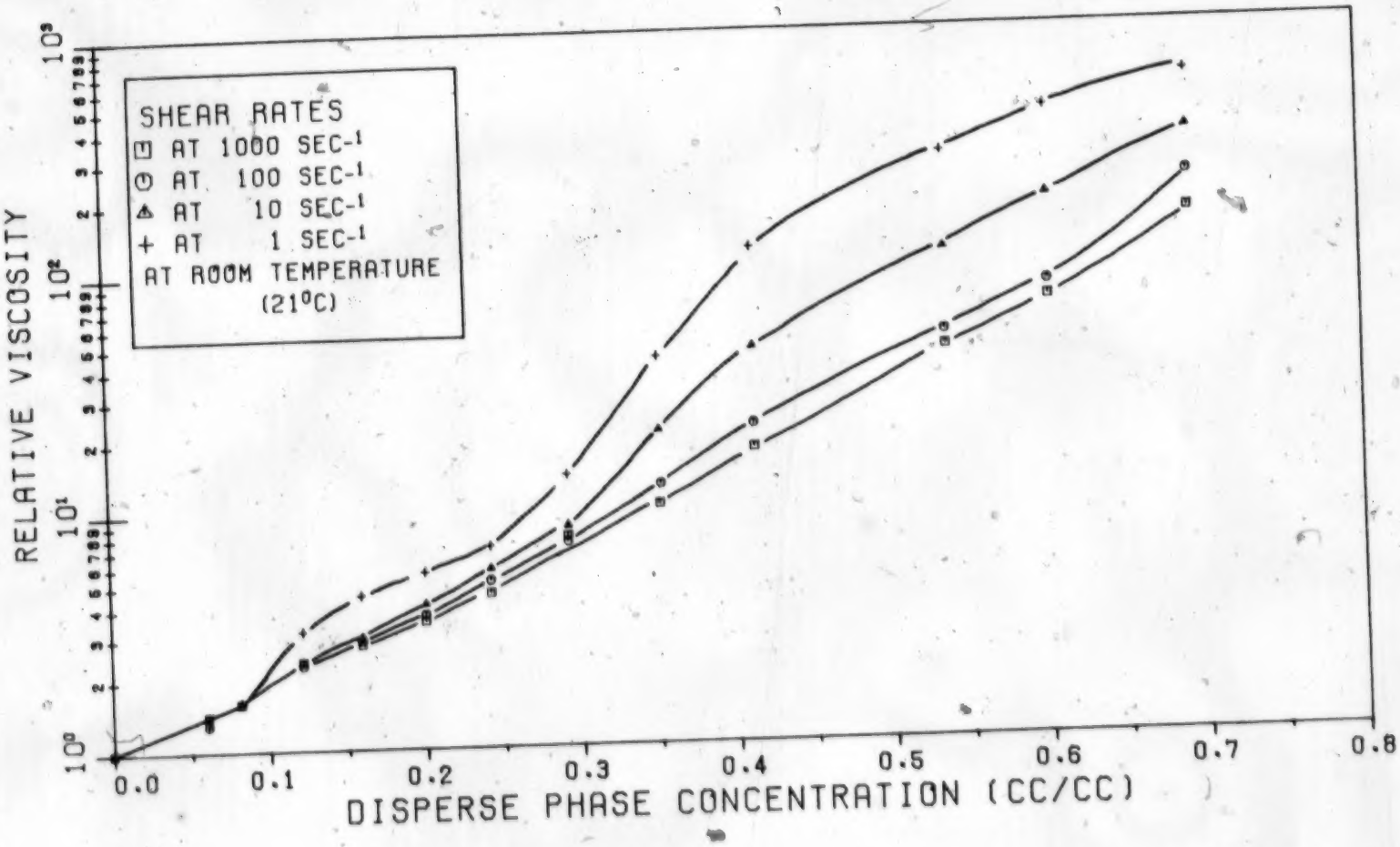

FIGURE A.20 - O/W EMULSION CORRELATION
EPPING CRUDE OIL

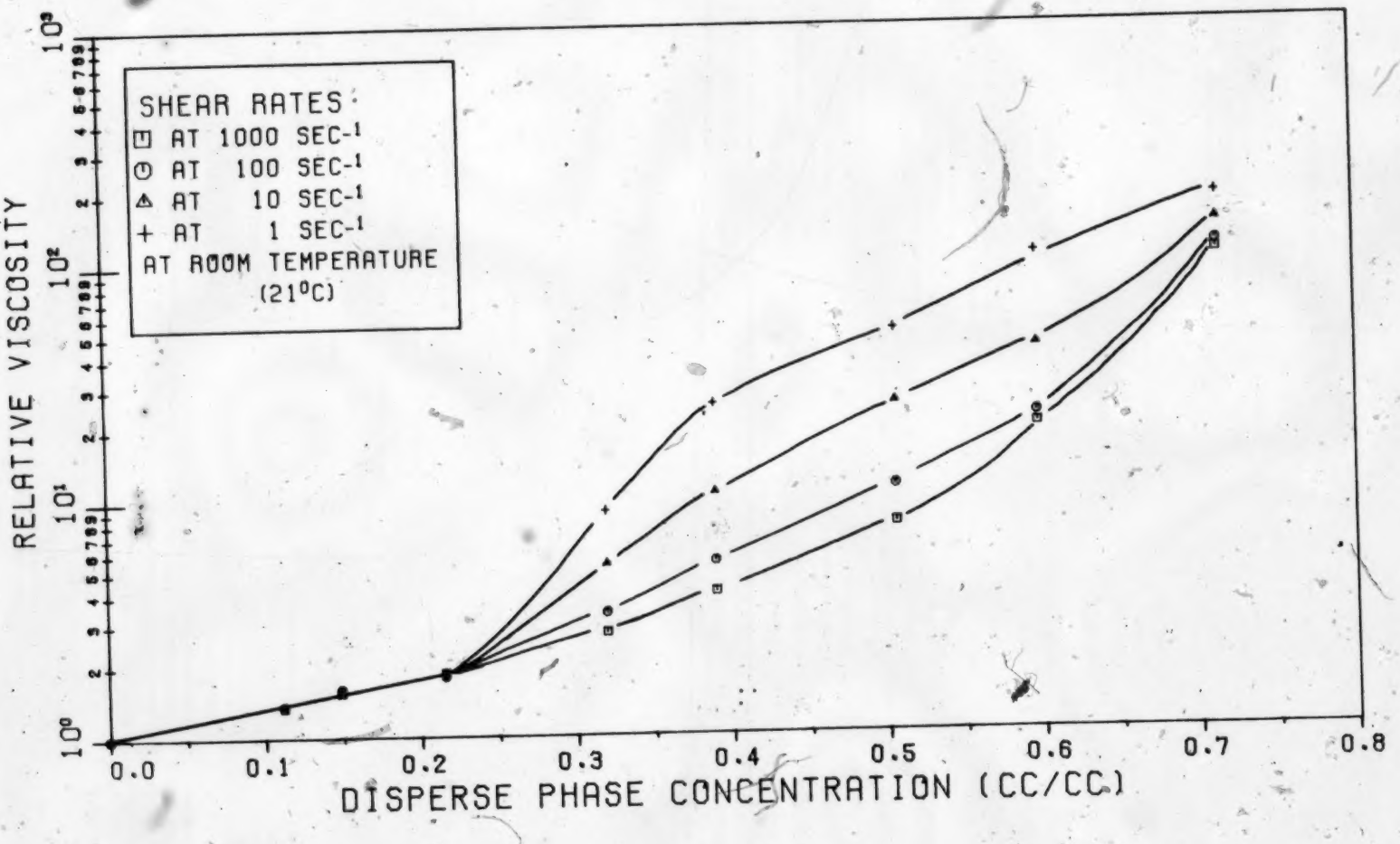

FIGURE A.21 - O/W EMULSION CORRELATION
COLD LAKE CRUDE OIL

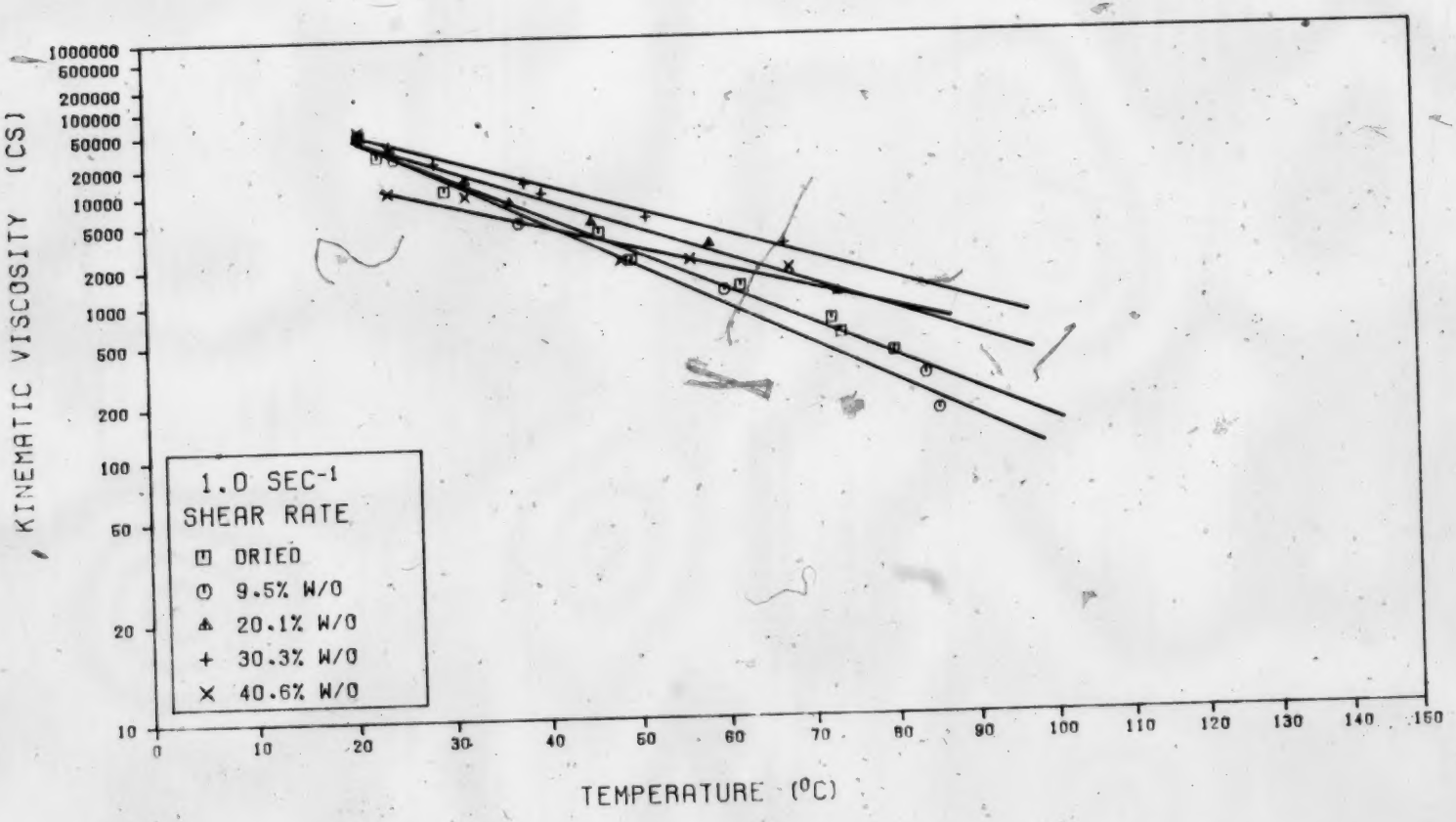

FIGURE A.22 - TEMPERATURE EFFECTS OF EPPING EMULSIONS AT A SHEAR RATE OF 1.0 1/SEC

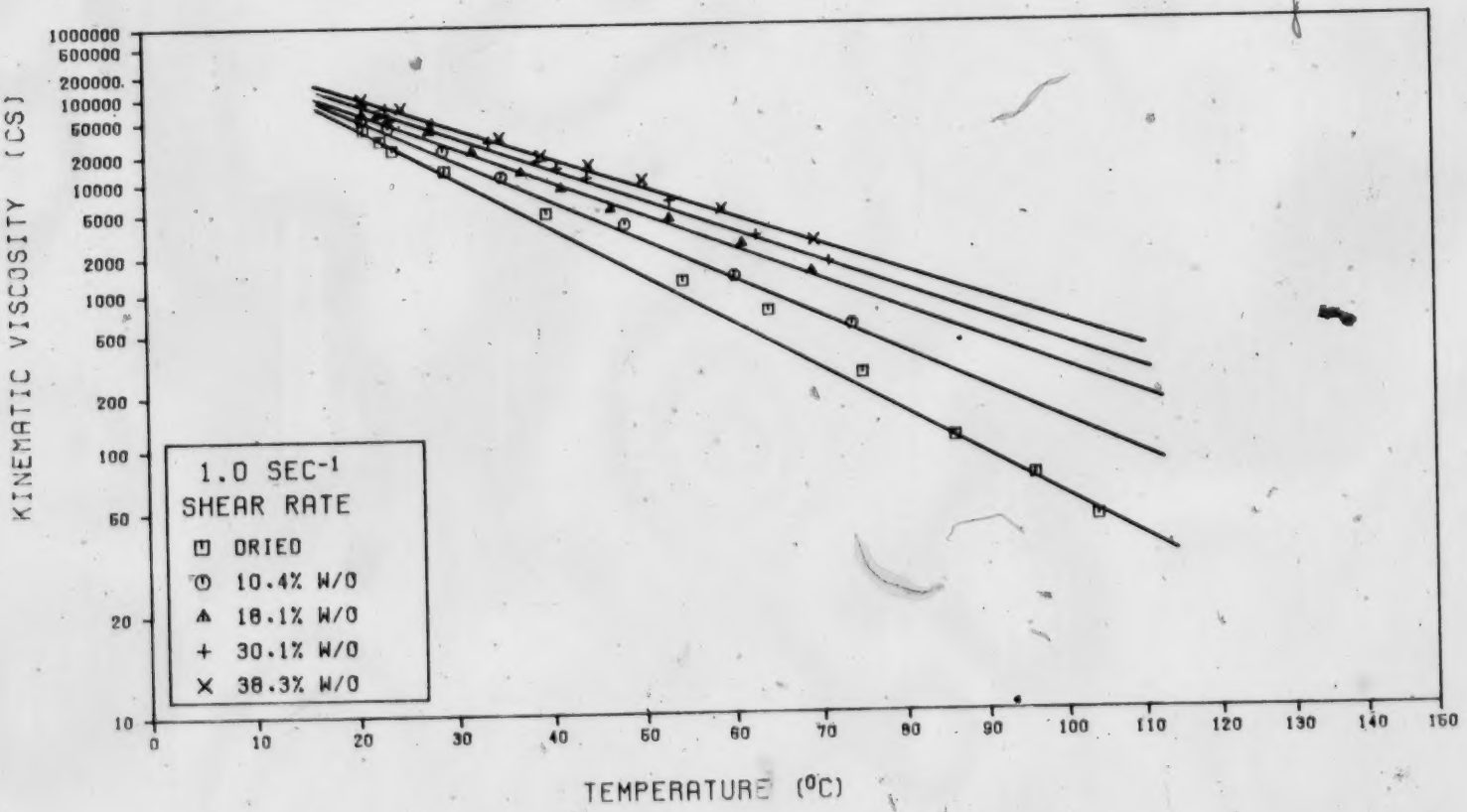

FIGURE A.23 - TEMPERATURE EFFECTS OF COLD LAKE EMULSIONS AT A SHEAR RATE OF 1.0 1/SEC

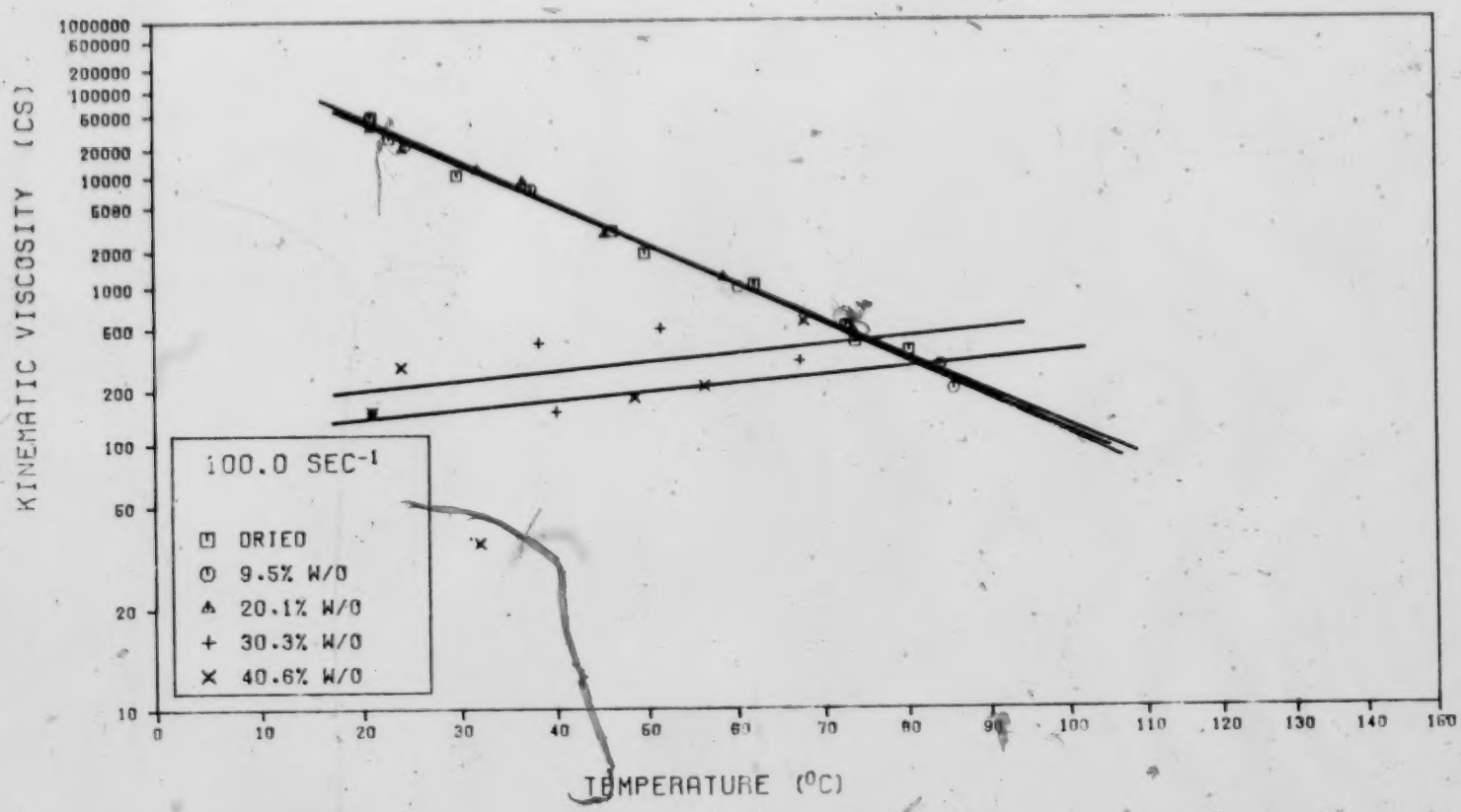

FIGURE A.24 - TEMPERATURE EFFECTS ON EPPING EMULSIONS AT A SHEAR RATE 100.0 1/SEC

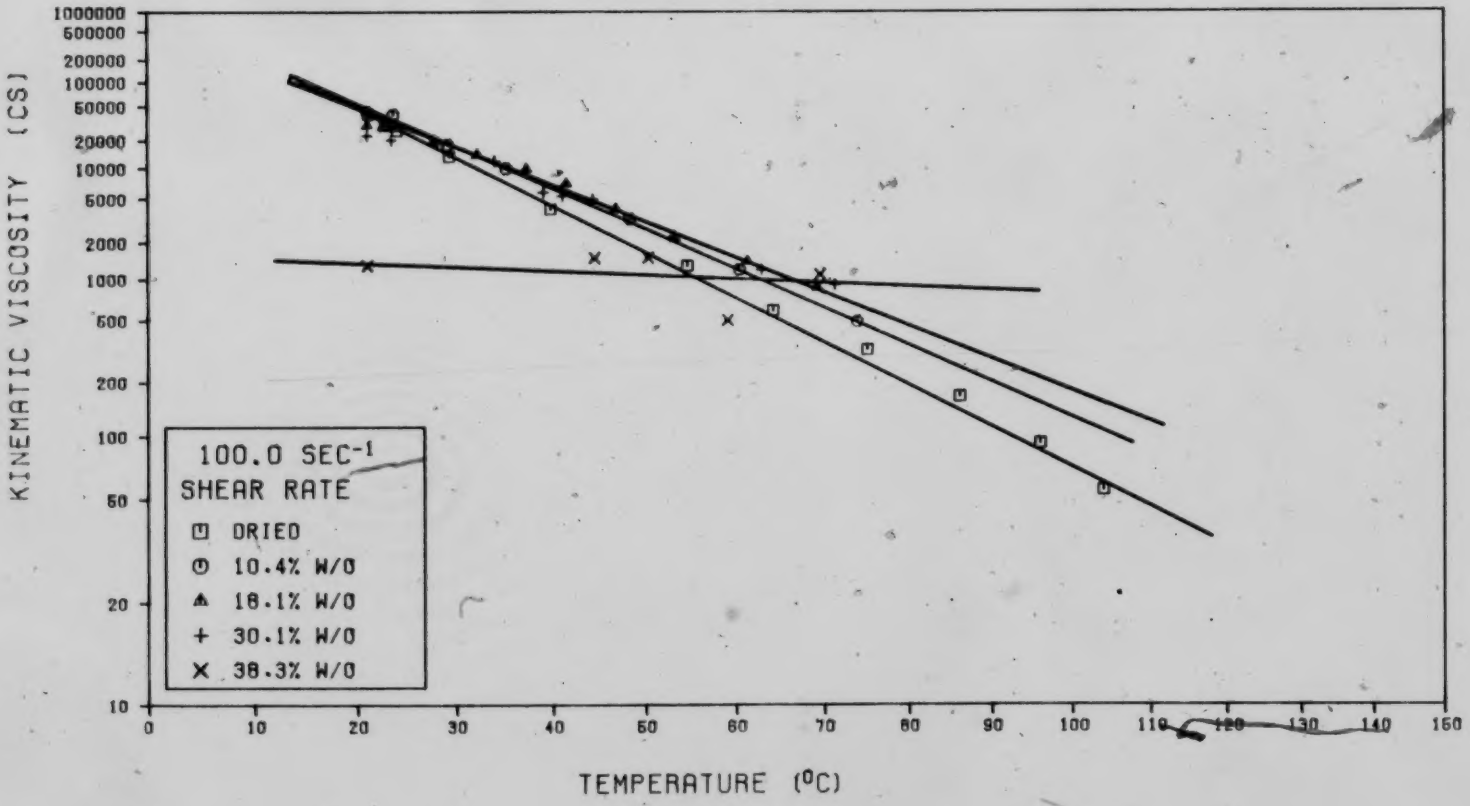

FIGURE A.25 - TEMPERATURE EFFECTS ON COLD LAKE EMULSIONS AT A SHEAR RATE OF 100.0 1/SEC

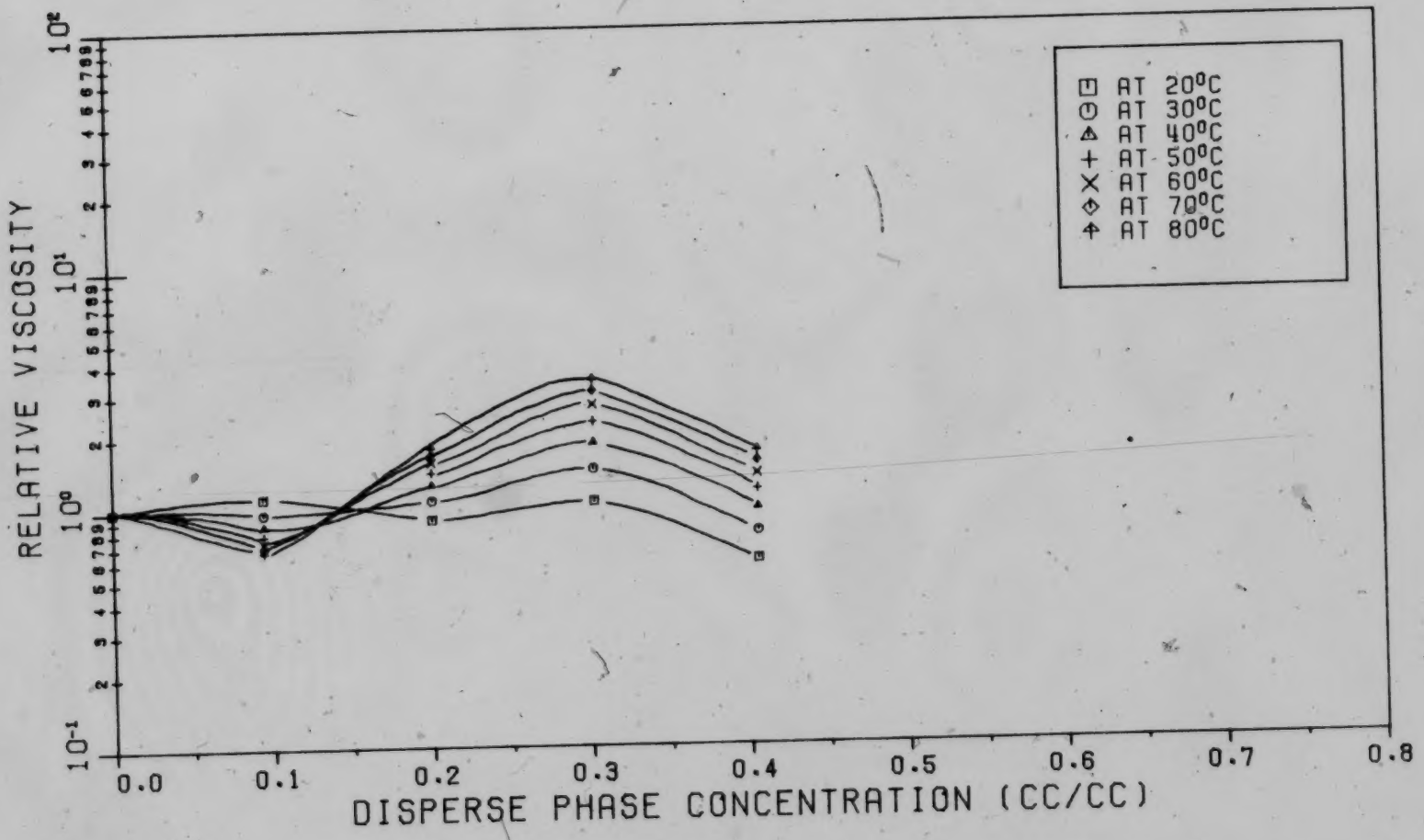

FIGURE A.26 - EPPING W/O EMULSION CORRELATION AT A SHEAR RATE OF 1.0 1/SEC

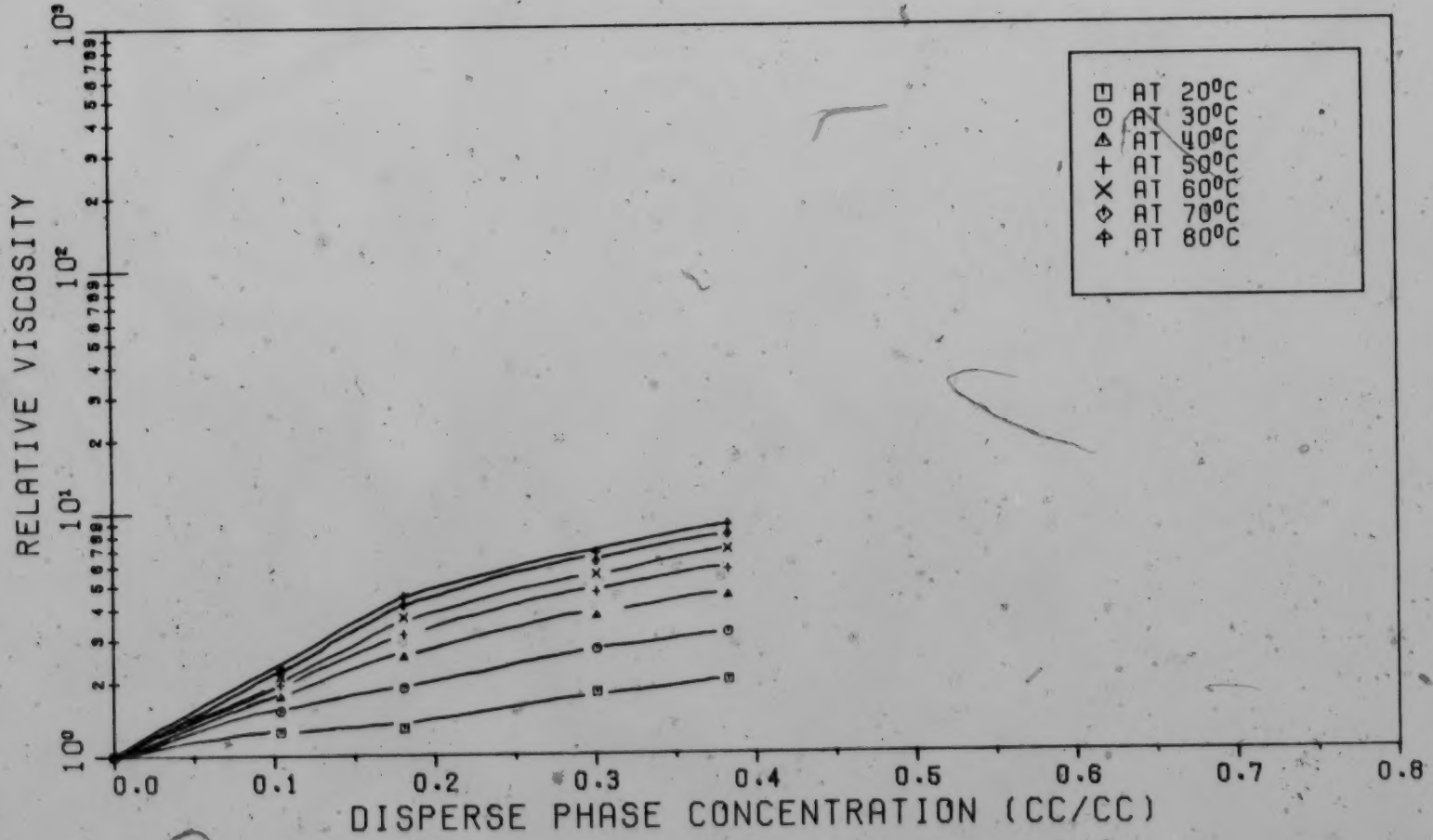

FIGURE A.27 - COLD LAKE W/O EMULSION CORRELATION AT A SHEAR RATE OF 1.0 1/SEC

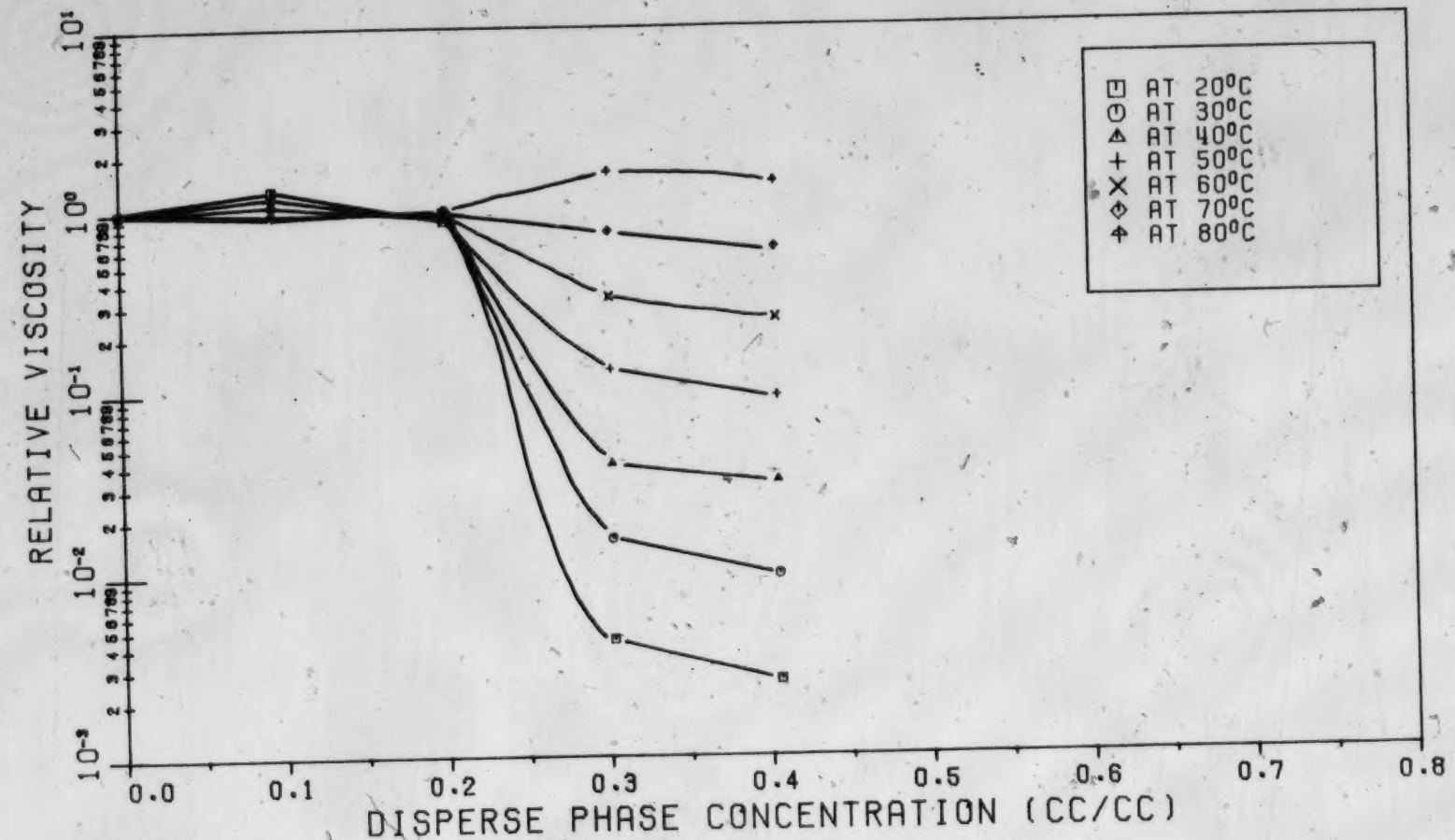

FIGURE A.28 - EPPING W/O EMULSION CORRELATION AT A SHEAR RATE OF 100.0 1/SEC

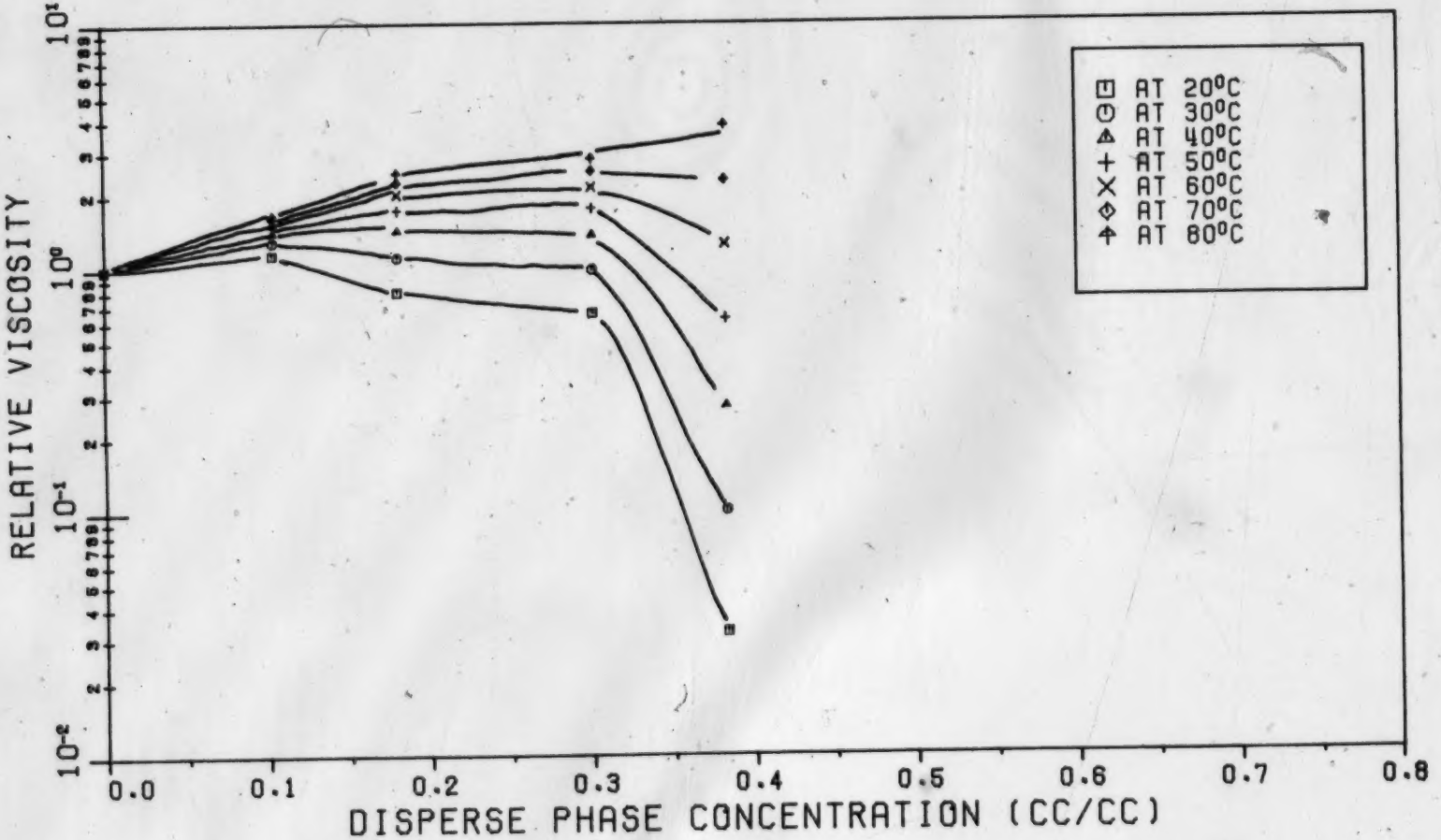

FIGURE A.29 - COLD LAKE W/O EMULSION CORRELATION AT A SHEAR RATE OF 100.0 1/SEC

APPENDIX B

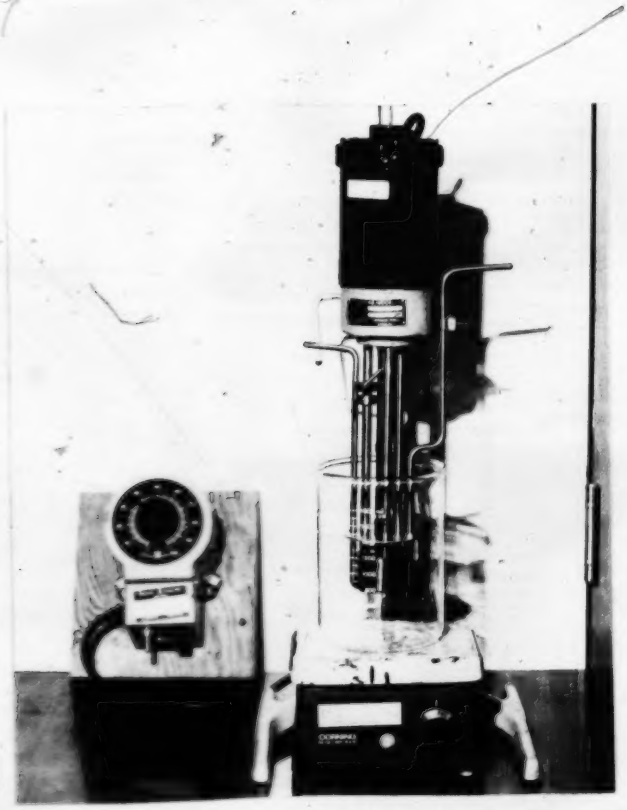

Plate B.1 Gifford-Wood Homogenizer 1-LV

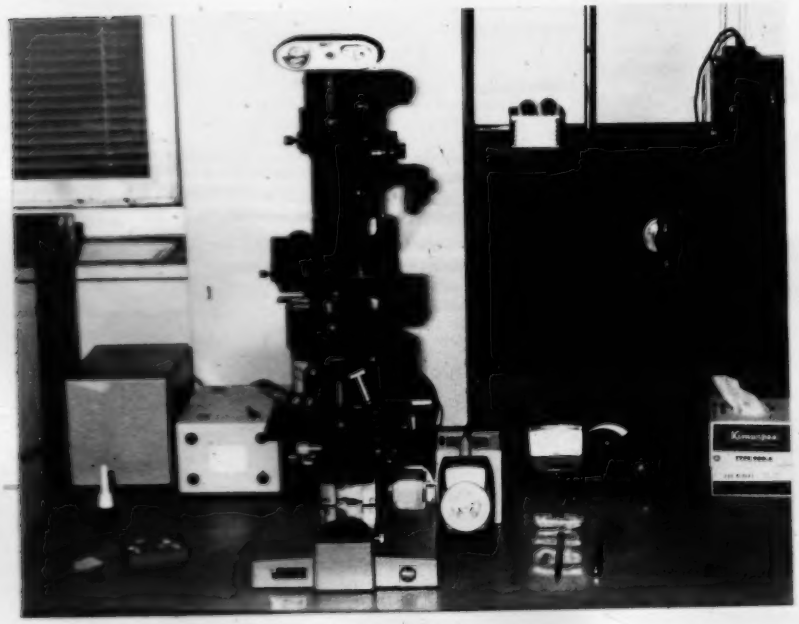

Plate B.2 Emulsion Photography Equipment

Plate B.3 Anton Paar Densitymeter DMA60 amd DMA512

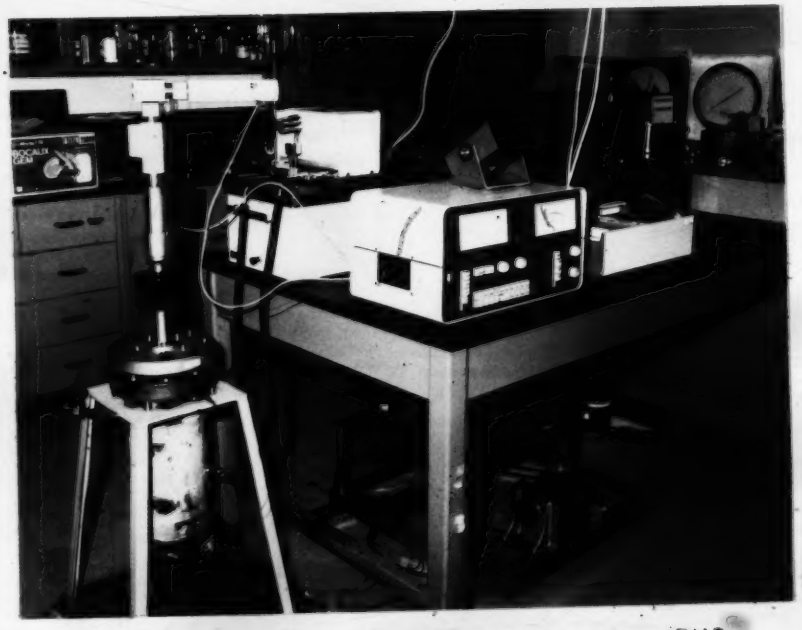

Plate B.4 Haake Rotovisco Viscometer RV3, Heating Bath and X-Y Plotter

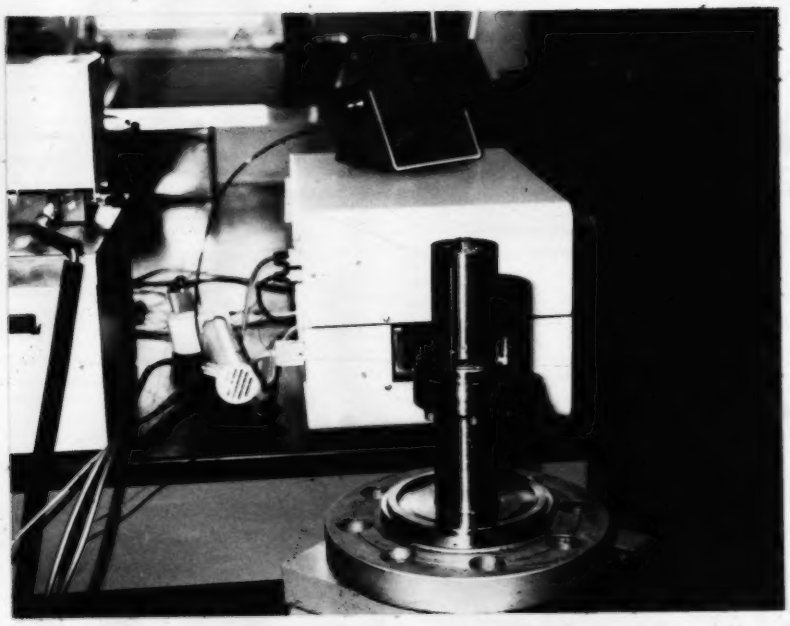

Plate B.5 Haake Viscometer EF Measuring Head.
Note: vertical slits allow fluid circulation

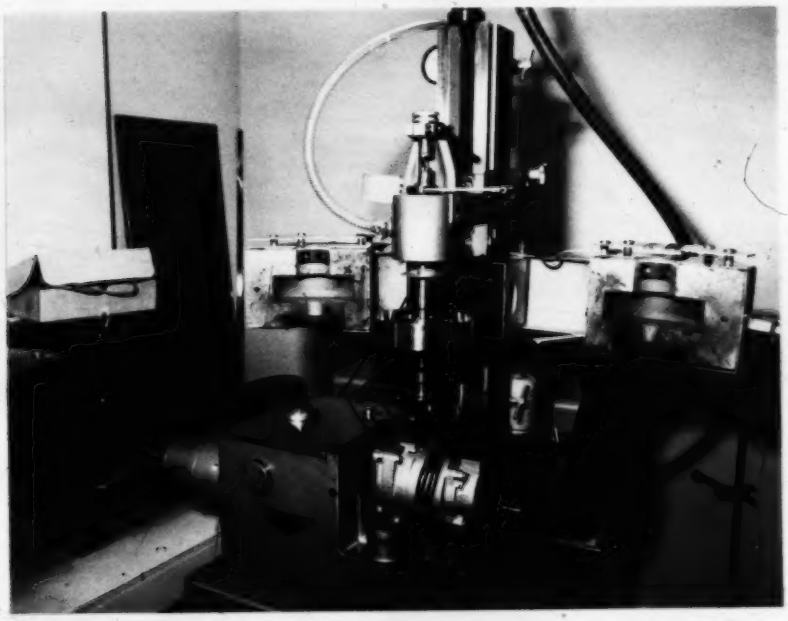

Plate B.6 Weissenberg Pheogoniometer R18

Plate B.7 Weissenberg Cone and Plate Measuring Head
Note: the small flat cylinder holds 50cc of sample fluid, while only 2cc of fluid is actually sheared between the cone and plate.

APPENDIX C

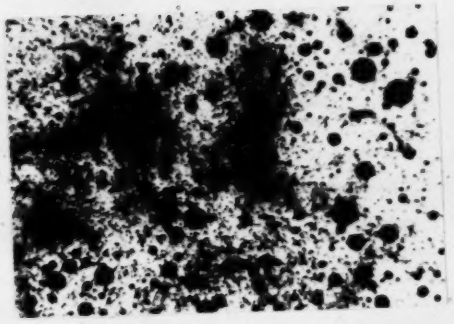

Plate C.1
14.9% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

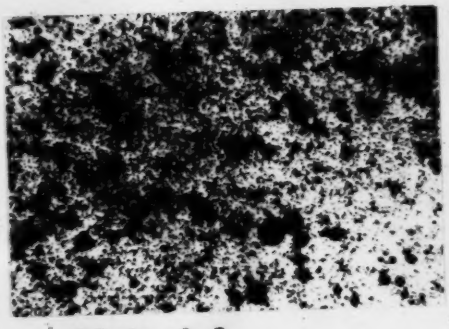

Plate C.2
21.6% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

Plate C.3
32.0% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

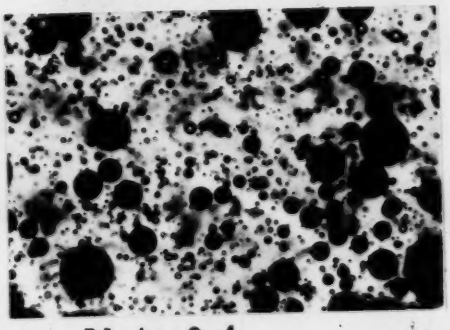

Plate C.4
39.0% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

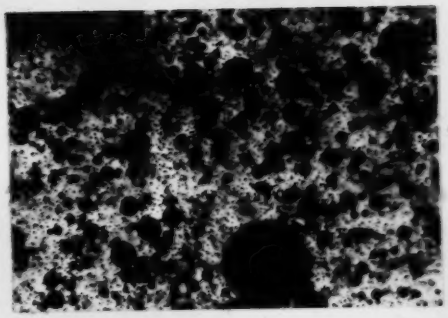

Plate C.5
39.0% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

Plate C.6
50.6% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

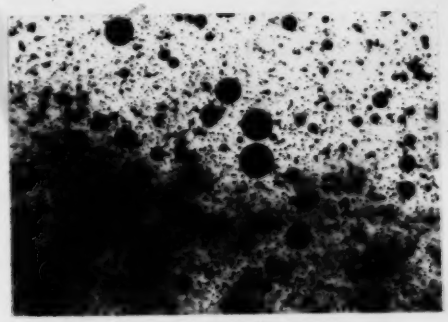

Plate C.7
59.7% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

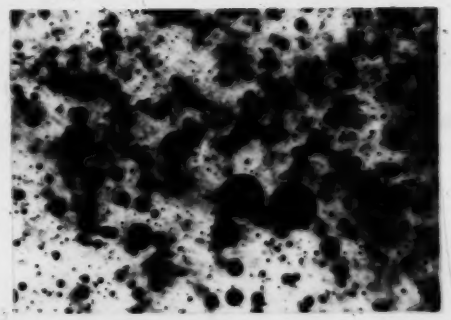

Plate C.8
71.3% Cold Lake
Oil-in-Water Emulsion
Magnification 1790X

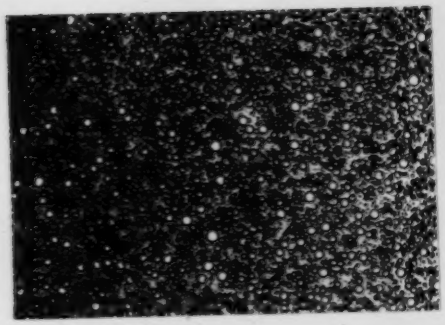

Plate C.9
18.1% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

Plate C.10
18.1% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

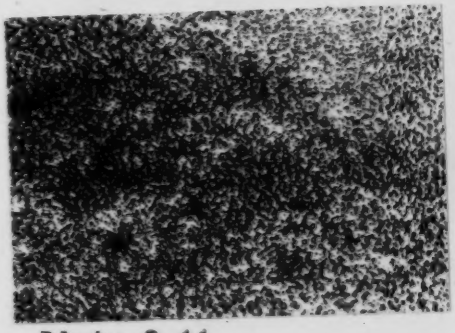

Plate C.11
30.1% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

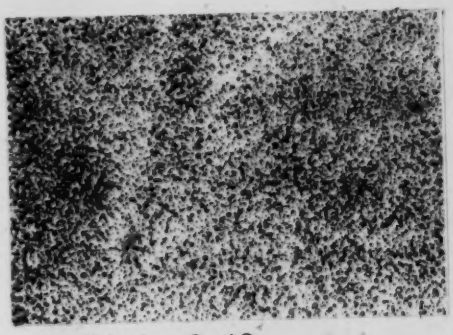

Plate C.12
30.1% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

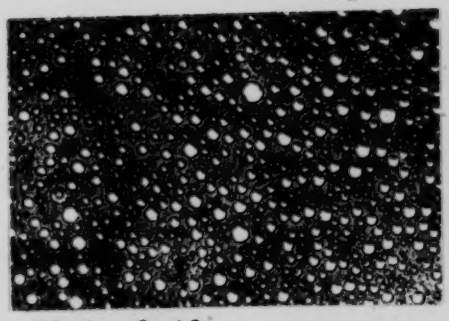

Plate C.13
38.3% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

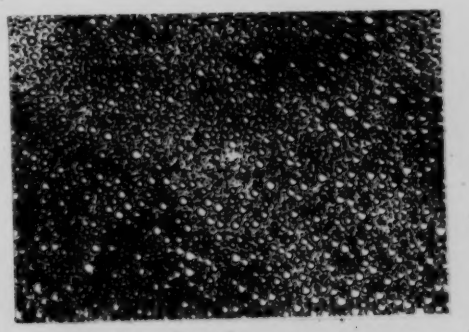

Plate C.14
38.3% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

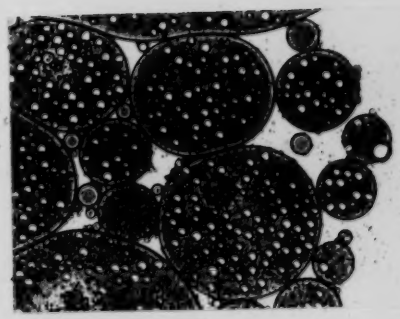

Plate C.15
38.3% Cold Lake
Water-in-Oil Emulsion
Magnification 7450X

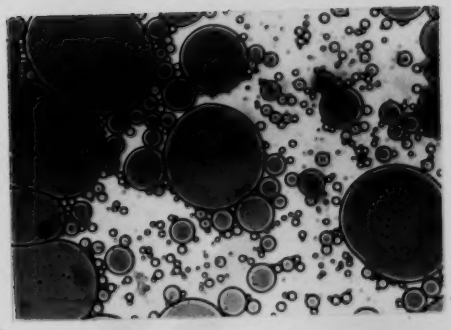

Plate C.16
12.2% Epping
Oil-in-Water Emulsion
Magnification 7450X

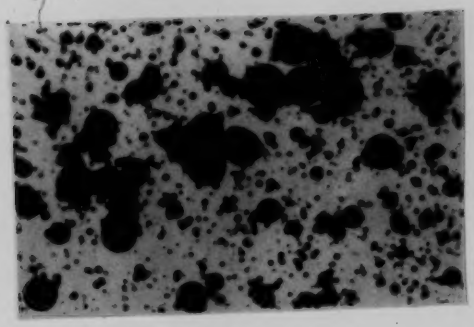

Plate C.17
12.2% Epping
Oil-in-Water Emulsion
Magnification 7450X
(after 1 week storage)

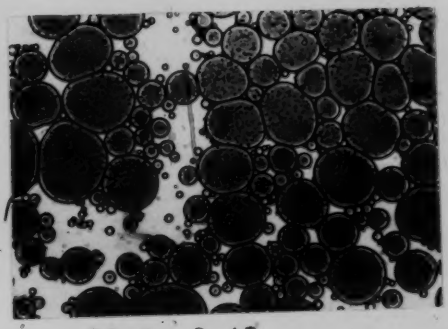

Plate C.18
20.1% Epping
Oil-in-Water Emulsion
Magnification 7450X
(after formation)

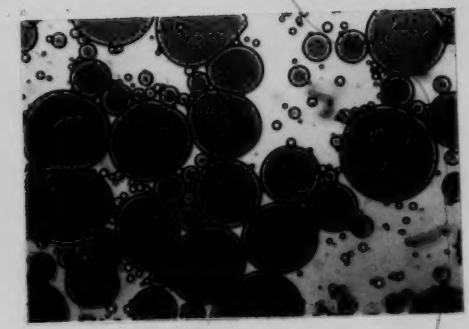

Plate C.19
20.1% Epping
Oil-in-Water Emulsion
Magnification 7450X
(after 1 week storage)

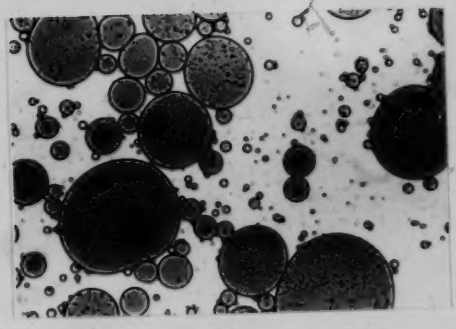

Plate C.20
20.1% Epping
Oil-in-Water Emulsion
Magnification 7450X
(after 3 weeks storage)

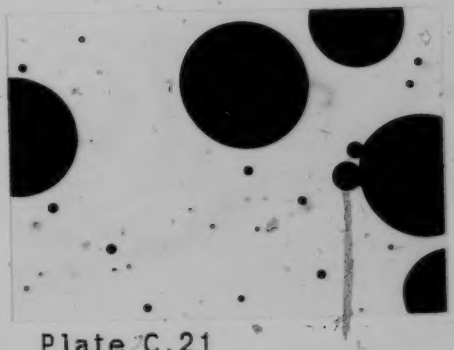

Plate C.21
53.6% Epping
Oil-in-Water Emulsion
Magnification 7450X

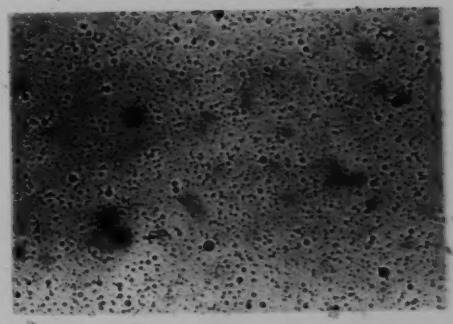

Plate C.22
9.5% Epping
Water-in-Oil Emulsion
Magnification 7450X

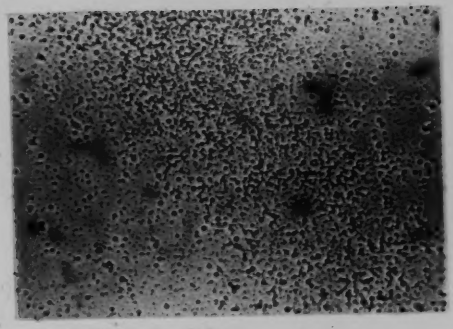

Plate C.23
9.5% Epping
Water-in-Oil Emulsion
Magnification 7450X
(after experiment)

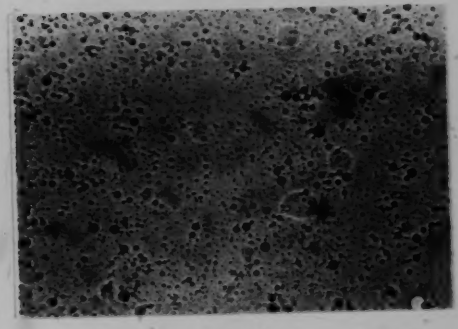

Plate C.24
30.3% Epping
Water-in-Oil Emulsion
Magnification 7450X
(after formation)

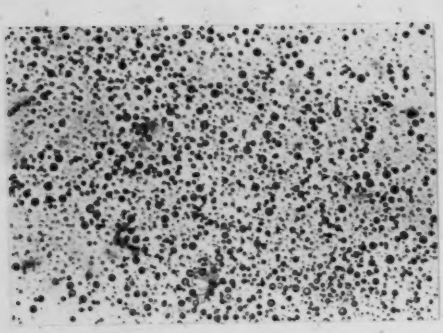

Plate C.25
40.6% Epping
Water-in-Oil Emulsion
Magnification 7450X
(after formation)